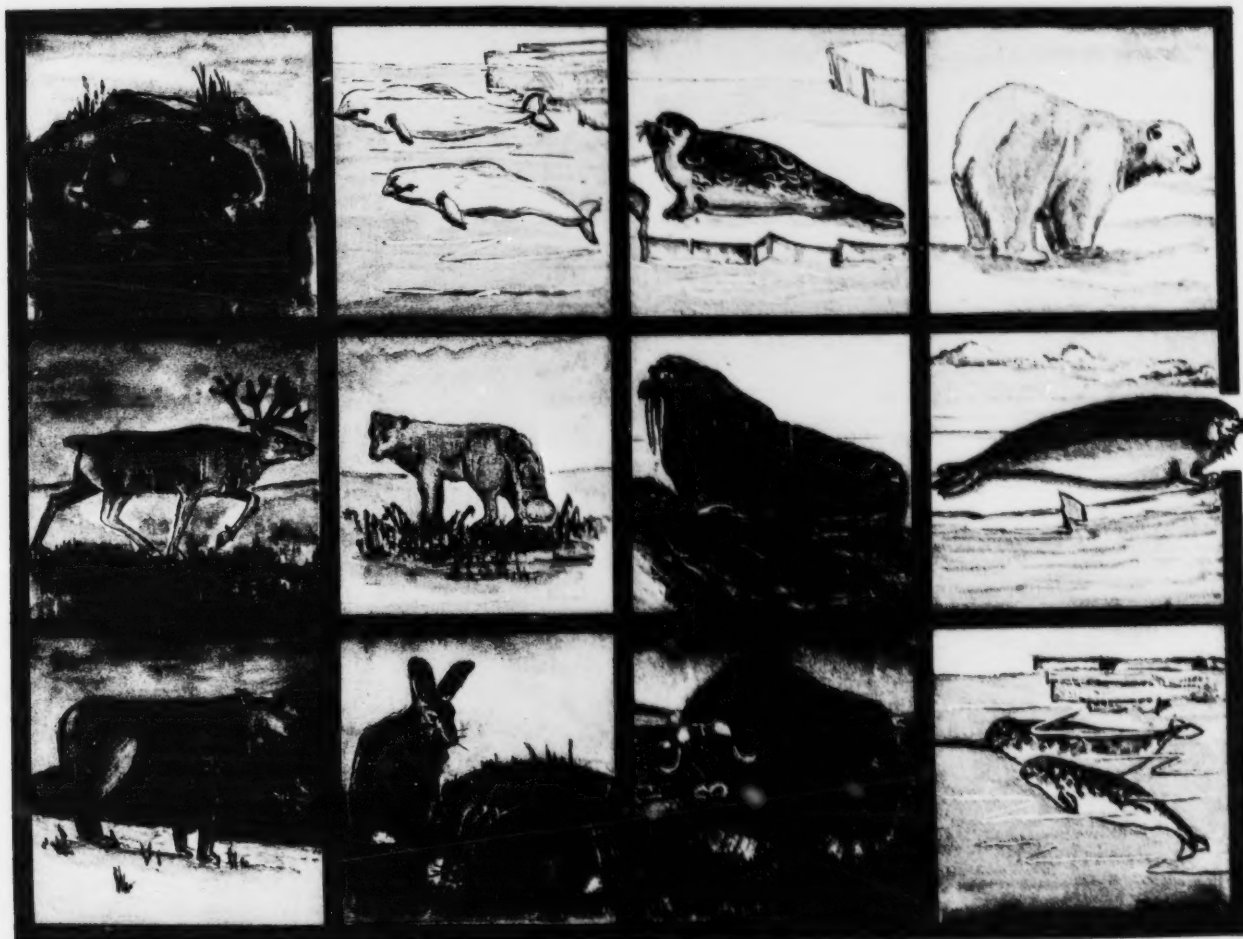


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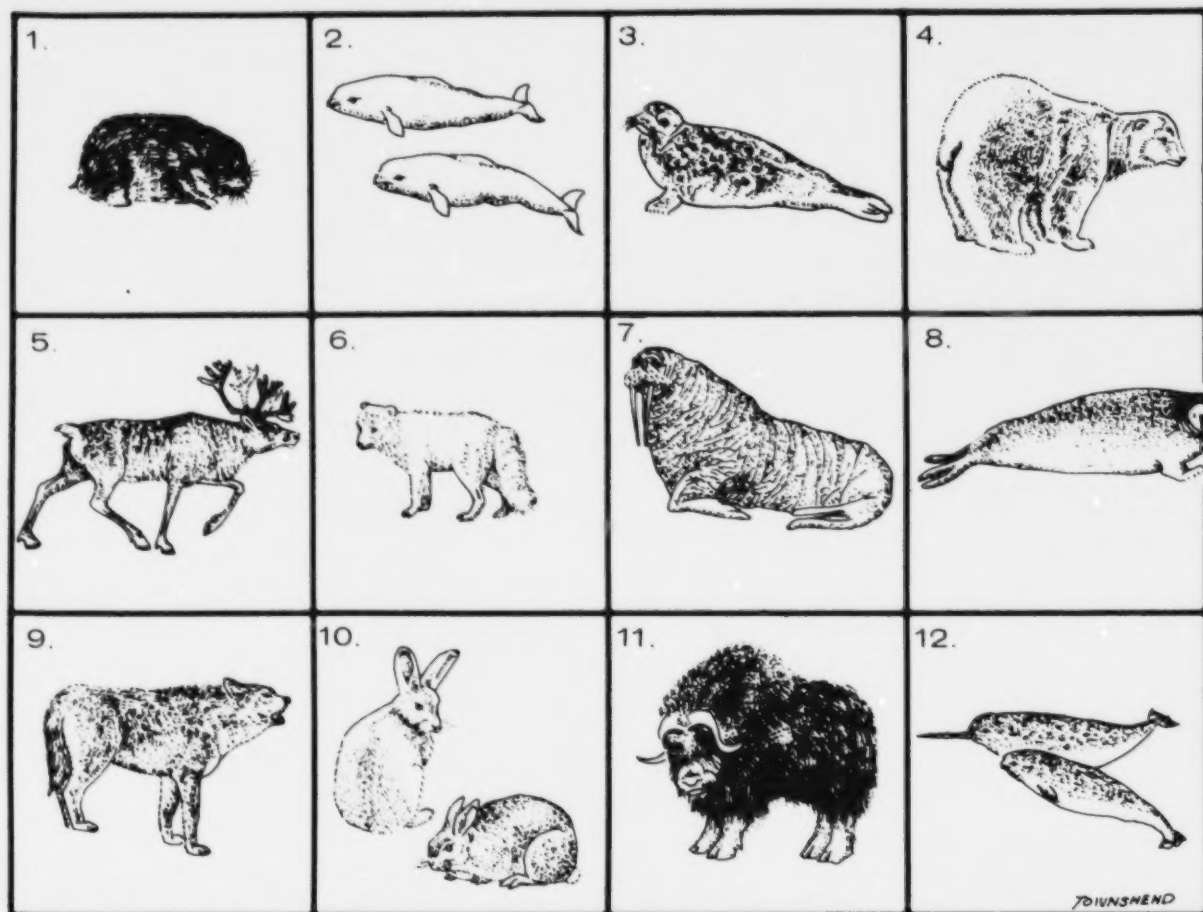
PROCEEDINGS OF THE NINTH ARCTIC MARINE OILSPILL PROGRAM TECHNICAL SEMINAR



JUNE 10-12, 1986

EDMONTON, ALBERTA

MAMMALS OF THE ARCTIC



- | | |
|-------------------------|--|
| 1. LEMMING | <i>Dicrostonyx groenlandicus</i> |
| 2. WHITE WHALE (Beluga) | <i>Delphinapterus leucas</i> |
| 3. RINGED SEAL | <i>Phoca hispida</i> |
| 4. POLAR BEAR | <i>Ursus maritimus</i> |
| 5. CARIBOU | <i>Rangifer tarandus groenlandicus</i> |
| 6. ARCTIC FOX | <i>Alopex lagopus</i> |
| 7. WALRUS | <i>Odobenus rosmarus</i> |
| 8. BEARDED SEAL | <i>Erignathus barbatus</i> |
| 9. WOLF (Grey) | <i>Canis lupus</i> |
| 10. ARCTIC HARE | <i>Lepus arcticus</i> |
| 11. MUSKOX | <i>Ovibos moschatus</i> |
| 12. NARWHAL | <i>Monodon monoceros</i> |

● Mammal names follow Banfield (1974). Mammals of Canada.

● Graphics by B.A.K. Townshend. (E.P.S., Environment Canada)

PROCEEDINGS OF THE NINTH ANNUAL
ARCTIC AND MARINE OILSPILL PROGRAM
TECHNICAL SEMINAR

Seminar Sponsored by:
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June 10-12, 1986
Edmonton, Alberta

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DATA ON THE CHARACTER OF ASPHALT PAVEMENTS

E.H. Owens, W. Robson and B. Humphrey*

ABSTRACT

Asphalt pavements have been observed and studied on beaches in mid- and high-latitudes following several spills. This discussion relates data from the BIOS experimental spill to real-world data from the "Amoco Cadiz" and "Metula" spills. A pavement is defined as a stable mixture of stranded oil and sediments that is anchored onto a beach surface. They form either on the beach face, usually above the neap high-water mark, or on low-tide terraces, on well-drained substrates which do not have a steep gradient nor a high ground-water table, and which are protected to some degree from high-energy coastal processes. Having formed, pavements can persist for long periods of time: 5 to 10 years, perhaps even longer.

Total hydrocarbon results from pavement samples show a marked consistency in concentrations through time. This is not unrealistic as concentrations in a stable feature would not be expected to change significantly if the physical character of the pavement does not change. A trend of lower oil concentration values on low-tide terrace pavements, as compared to beach-face pavements, was also evident. Differences in oil concentrations between locations are considered to be function of loading. The maximum loading of the BIOS beaches ranged between 10,000 and 60,000 mg/kg. Higher loadings would be expected in areas where fine-grained sediments (i.e. sand) are less predominant, as these would fill much of the interstitial spaces on pebble beaches. Oil concentrations on two beaches with similar sediments had similar oil-in-sediment concentrations (Punta Espora, Chile - 22,000 mg/kg; Cape Hatt, Canada - 19,000 mg/kg).

The GC results show that samples from the lower intertidal zone were more weathered than those from upper beach and backshore locations. The evaporative weathering occurred primarily within one year following the spill. The data also show that where oil remains in high concentrations, as is common in a pavement, the SHW and ALK/ISO ratios remain higher, indicating that lower weathering rates are associated with high oil concentrations.

At the "Amoco Cadiz" sites a "latex" oil mat was sampled on fine-grained mud flats and marshes. This oil had weathered similarly to the pavement oils found nearby. It is likely that the same oil may form a mat cover on fine sediments and an asphalt pavement on coarse sediments.

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INTRODUCTION

The presence of asphalt pavements on the shore following marine or coastal spills has been reported by a number of observers. In the recent BIOS (Baffin Island Oil Spill) Project, an experimental release of 15m³ of Lagomedio crude into the nearshore environment resulted in heavy shoreline contamination and the subsequent formation of an asphalt pavement. Data from this experiment are compared with other published information to identify common factors in the formation and character of asphalt pavements.

DEFINITION

An asphalt pavement has been defined (Owens and Robson, 1985) as a stable mixture of weathered hydrocarbons and sediments that, through time and physical changes, has formed a persistent and erosion-resistant deposit that is anchored onto a beach surface.

BACKGROUND TO DATA SETS

(a) "Metula" - Southern Chile

The VLCC "Metula" ran aground on 9 August, 1974 near the First Narrows of the Strait of Magellan. Between the time of the grounding and 25 September, an estimated 52,300 tons of light Saudi Arabian crude oil and 2,000 tons of Bunker C were spilled (Gunnerson and Peter, 1976). The oil contaminated approximately 250 km of coast by the time of a shoreline survey conducted in February 1976 (Blount, 1978). This shoreline survey and the associated sample collection and analysis project, conducted 32 months after the initial grounding, provides data on the areal extent of the asphalt pavements and on the oil content of the contaminated sediments (Blount, 1978). Oil was extracted from a 100gm oil-sediment sample over 24 hours using a methanol-benzene solvent. Sediment size had to be less than 5.5cm diameter, the size of the soxhlet extraction tube. All the results were converted from weights of oil and of clean sediment to a per cent volume. For this discussion, the volumetric percentages were converted back to oil-in-sediment by weight values so that direct comparisons could be made with results from studies conducted by the authors.

(b) BIOS, Cape Hatt, Baffin Island, Northern Canada

An experimental release of 15m³ of weathered Lagomedio crude oil was carried out on 19 August, 1981 in the nearshore at Cape Hatt, Baffin Island, N.W.T.. An estimated 5m³ of the oil was stranded initially over a 300m length of intertidal beach (Owens et al., 1986). Surveys and sampling were conducted in 1983 and 1985 on an intertidal asphalt pavement that had formed between September 1982 and August 1983. The results reported in this discussion are based on samples collected on 9 August, 1985. The period August 1981 to August 1985 included an estimated 12 months of open-water conditions in this ice-dominated marine environment. This period of approximately 12 open-water months after the release is used for comparison with lower latitude (ice-free) coastal environments (Owens, Hope and Humphrey, 1986).

(c) "Amoco Cadiz" - Northwest France

The VLCC "Amoco Cadiz" ran aground on the Brittany coast of France on 16 March, 1978 and a total of 223,000 metric tons of oils and a small amount of Bunker C was spilled. An estimated 62,000 tons was stranded on the adjacent shore and by April, 1978 about 320 km of coast was contaminated. By November, 1979 oil remained along only 50 km of coast (Berne and D'Ozouville, 1979; Gundlach, et al., 1981). A shoreline survey conducted by J. Denis of CEDRE in autumn 1984 indicated that a few kilometres of "Amoco Cadiz" oil remained on the coast (pers.comm; 1984). All of the oiled sites located by J. Denis were visited in March 1985, 84 months after the spill, and samples were collected for total hydrocarbon and GC analyses (Owens and Robson, 1985). The extraction and analytical procedures were identical to those used for the BIOS project (Hope and Humphrey, 1986).

OBSERVATIONS AND TOTAL HYDROCARBON DATA

(a) "Metula"

The results from this spill represent the "youngest" data set considered in this discussion. Blount's study (1978) was conducted 32 months after the spill and extensive asphalt pavements had formed on the beach-face and the low-tide terrace sections of mixed sediment (sand and gravel) beaches at a variety of locations in the Straits of Magellan, east of the Second Narrows. A more recent survey, 78 months after the spill (Gundlach et al., 1982), showed that the majority of these pavements were still present and were up to 15-cm thick.

Data from Blount's study yield mean values of oil-in-sediment by weight of 47,350 mg/kg for the beach face samples and 18,400 mg/kg for the low-tide terrace samples (Table 1). Although there is a wide range of individual values, up to an order of magnitude, approximately half of the 39 samples analysed were in the range 20,000 to 50,000 mg/kg. The range of values can be explained in part by variations in sediment type between the pavement sites.

(b) BIOS

The Bay 11 asphalt pavement was first observed in 1983 (Owens, 1984) and was resurveyed and resampled in 1985 (Owens, Hope and Humphrey, 1986). The characteristic feature of the intertidal zone during 1983 was the presence of a large asphalt pavement on the beach in the upper intertidal zone with a secondary smaller pavement associated with a gravel ridge in the lower intertidal zone (Figure 1)(see Figures 5.5 and 5.6 in Owens, Hope and Humphrey, 1986). The approximate area of the pavement was 325m² and the thickness varied between 3 and 10 cm. An estimate of the volume of oil contained in the asphalt pavement produces a value of 0.73m³ (Owens et al., 1986). The asphalt pavement in 1983 contained approximately half of the total estimated volume of oil that remained in the beach. This oil volume was in the order of 5% of the original oil that was spilled and covered 15% of the shoreline that was originally oiled in 1981.

Table 1. "Metula" Asphalt Pavement Data : 1976 (After Blount, 1978)

LOCATION	NUMBER OF SAMPLES	MEAN VALUE	CONVERTED VALUE (mg/kg)
(a) Beach Face			
Punta Espora	8	6.9%	22,000 mg/kg
Banco Orange (MT-7)	4	5.9	18,750
Banco Orange (MT-5)	5	21.6	68,000
Banco Lomas	<u>7</u>	<u>25.2</u>	<u>80,000</u>
Mean	24	15.0	47,350
(b) Low-Tide Terrace			
Punta Espora	3	5.0%	16,000 mg/kg
Punta Baxa	1	9.9	31,500
Punta Anegada	4	3.7	12,000
Bahía Azul	<u>1</u>	<u>4.6</u>	<u>14,500</u>
Mean	9	5.8	18,400

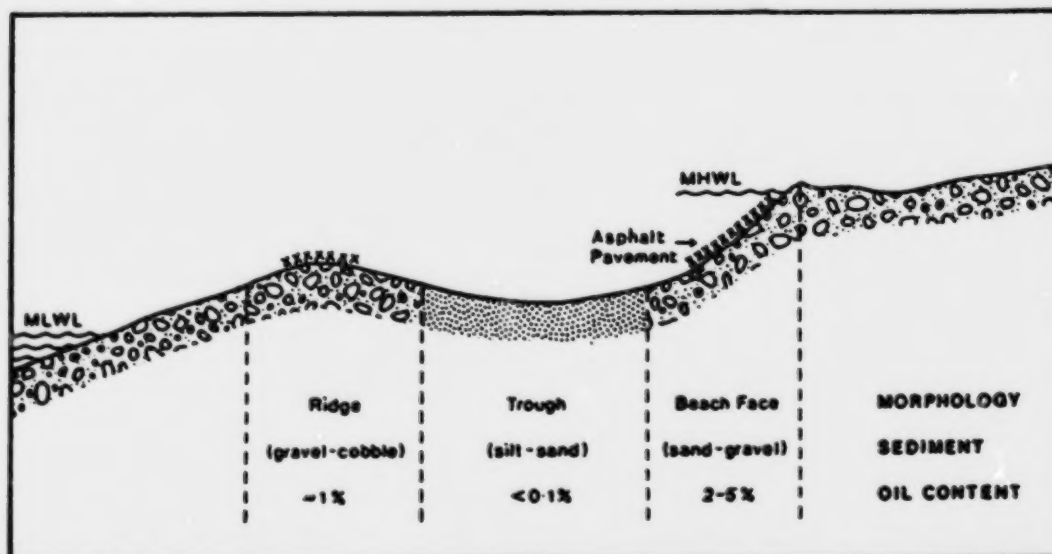


Figure 1. Schematic diagram to show location of asphalt pavement in the intertidal zone at Bay 11, Cape Hatt; and to illustrate the relationship between beach morphology, sediment type and oil concentrations (expressed as per cent oil-in-sediment by weight).

The 1985 data are considered to represent the effects of active intertidal processes over a 12-month open-water period (Owens *et al.*, 1986). By the time of the 1985 survey, the area of the pavement had been reduced to 205m², with an estimated oil volume of 0.3m³. The estimated total oiled area and the oil volume of the study beach did not change significantly between 1983 and 1985. It was apparent that the pavement was considerably "softer" and more mobile in 1985 and it is interpreted that the lack of change in the oiled area and oil volume between 1983 and 1985 is due to erosion of the pavement and the associated distribution of the released oil.

The total hydrocarbon analyses yield values that are higher on the beach face as compared to the ridge on the low-tide terrace (Table 2). The mean of the samples collected from the primary pavement on the beach face changed little between 1983 and 1985 (19,835 to 19,000 mg/kg). Two samples collected on the low-tide ridge in 1983 produced values of 500 and 9,750 mg/kg, compared to three 1985 sample values of 3,900, 6,400 and 24,400 mg/kg.

A backshore crude oil control plot, set up at Crude Oil Point in an adjacent bay in 1980, had initial total hydrocarbon concentrations in the range 34,000 to 66,000 mg/kg. This plot was unaffected by marine processes but by August 1985, 60 months after oiling, the mean oil-in-sediment by weight value had reduced to 16,000 mg/kg (Table 2). This data set provides a comparative baseline for the intertidal results in terms of weathering rates and processes.

(c) "Amoco Cadiz"

Two patches of beach-face pavement were sampled in 1985 in the vicinity of the mean high-water mark in the Ile Grande area, 84 months after the oil had become stranded (Owens and Robson, 1985). The total hydrocarbon concentrations of the samples ranged between 5,000 and 16,000 mg/kg (Table 3). In addition to the remnant pavement, a thin oil layer, similar to a latex mat, covered the sediments of the upper intertidal zone at two locations in Aber Benoit (see Photo. 6 in Owens and Robson, 1985) and on several marsh sections in the Ile Grande area. These mats were sampled and yielded values of 2,300 and 3,300 mg/kg. The mats were seen at Croix (Aber Benoit) and Ile Grande in low-energy mud flats and marsh environments respectively (Vandermeulen and Long (in prep.)). There was no indication at either site of oil penetration into the sediments and the coverage was continuous from the extreme upper intertidal (SHWM) through the MHW and as low as the Neap High Water Mark (NHWM). These mats completely covered large areas and vegetation was reported to have only recently begun to penetrate these sites (B. Long, pers. comm, 1985). The texture of the mats was quite rubbery and somewhat malleable in direct contrast to the pavements which were hard, dry and brittle.

G.C. ANALYSIS RESULTS

(a) BIOS

Samples collected in 1985 from the 1980 backshore control plot (T1) at Crude Oil Point, indicate that very little weathering had occurred since 1981, one year after the oil was laid down. In 1980, the gas chromatograms indicated weathering indices typical of fresh Lagomedio crude oil (Table 4). By 1981, these same indices showed that some weathering had occurred. Since then, very little change has taken place. The significant indices are the

Table 2. BIOS Asphalt Pavement Data : 1985

LOCATION	NUMBER OF SAMPLES	MEAN VALUE (mg/kg)	RANGE OF VALUES (mg/kg)
(a) Bay 11: Beach Face	6	19,000	12,000-25,000
(b) Bay 11: Low-Tide Terrace	3	11,600	3,900-24,400
(c) Crude Oil Point: Backshore	3	15,750	13,000-20,000

Table 3. "Amoco Cadiz" Asphalt Pavement Data : 1985

LOCATION	NUMBER OF SAMPLES	MEAN VALUE (mg/kg)	RANGE OF VALUES (mg/kg)
<u>(a) Beach Face</u>			
Toenot	3	5,500	4,900- 6,400
Ile Grande	6	9,300	6,100-16,000
<u>(b) "Latex" Samples</u>			
Aber Benoit	2	2,800	2,300- 3,300

Table 4. GC Results and Weathering Ratios From BIOS Backshore Control Plot (T1) : 1980-85

Sample	Concentration (Percent)	SHWR	ALK/ISO
(1) Aged Lagomedio Crude	Pure	2.3	2.5
(2) Surface Samples:			
1980	5.8%	2.3	2.1
1981	3.4	1.6	2.1
1985	1.6	1.6	2.0
(3) Subsurface Samples:			
1980	3.0	1.8-2.3	2.5-3.0
1981	2.1	1.7	2.5
1985	0.6	1.9	2.1

Table 5. GC Results and Weathering Ratios from BIOS Intertidal Asphalt Pavement : 1981-85 (All samples are from the surface of the beach in the intertidal zone of Bay 11)

Sample	Concentration (Percent)	SHWR	ALK/ISO
Profile 4 Upper, 1981	3.6	1.2	2.3
Profile 2 Upper, 1982	0.8	1.0	1.0
Profile 2 Upper, 1985	0.1	1.0	0.4
Profile 4 Upper, 1985	0.6	2.4	2.4
Profile 4 Lower, 1985	0.005	1.4	1.5

Saturated Hydrocarbon Weathering Ratio (SHWR), indicative of evaporative loss and biodegradation, and the Alkane/Isoprenoid Ratio (ALK/ISO), indicative of biodegradation. An examination of the chromatograms for the 1985 samples (Figure 2) supports the conclusions that little weathering has occurred since 1981. They have the appearance of slightly weathered crude oil. The indices and the chromatograms indicate that the subsurface sample is slightly less weathered than the surface sample, but as only one subsurface sample was analysed by GC a general conclusion is not possible.

Interpretation of the samples from Bay 11 results in similar conclusions. The oil was stranded on the beach in 1981, and lost the volatile components almost immediately. Subsequently, the observations may be classified into two types, one type typical of high oil concentration with weathering similar to the T1 backshore control plot, and the other typical of low oil concentration with more weathered oil showing signs of biodegradation.

The chromatograms of samples from the upper intertidal zone and lower intertidal zone on profile 4 are examples of these differences (Figure 4). The chromatogram of the high concentration (Profile 4) upper sample includes distinct, well-resolved alkanes from about C10 up, with a low UCM (unresolved complex mixture). The chromatogram of the low concentration sample from the (Profile 4) lower intertidal zone, although including some resolved alkanes, also includes a significant UCM and shows loss of alkanes relative to isoprenoids (Table 5).

An example of high concentration oil was found in the upper intertidal zone of Bay 11 in a set of the creek edge samples (Figure 3), which were about 2.7 percent oil on the surface and 1.2 percent oil 3-8cm down. The subsurface sample is slightly less weathered than the surface sample, and both are similar to the control T1 oil (Figure 2).

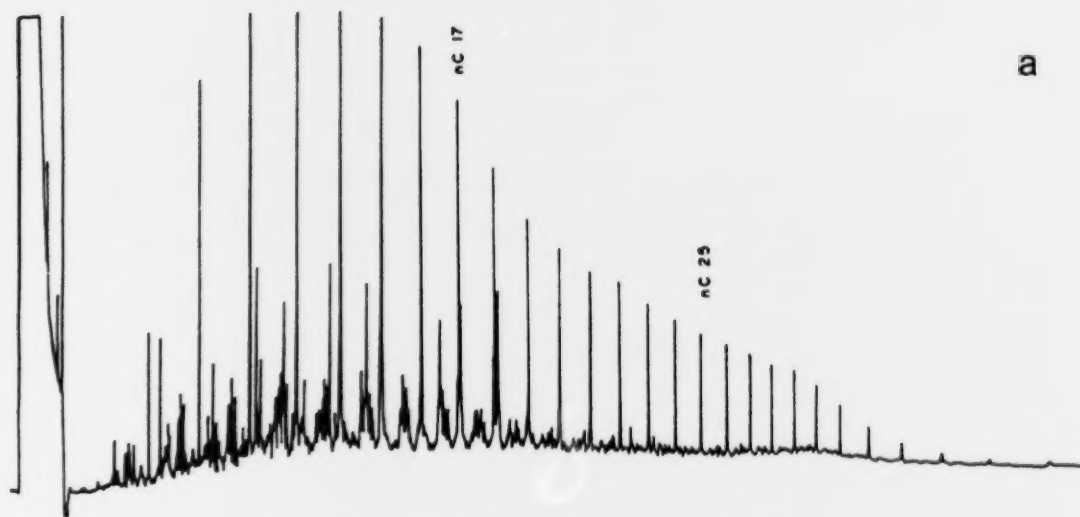
(b) "Amoco Cadiz"

For direct comparison to oil stranded in temperate areas, some samples from oil stranded after the "Amoco Cadiz" spill may be examined. The oil was stranded in the spring of 1978, and by 1979 was showing considerable weathering. Unfortunately, the data does not appear to be available in the general literature in the detail necessary for direct comparison to the BIOS data. Some general comments may be made. Almost all of the samples collected in the spring of 1985, show stage 4 weathering, as indicated by a large UCM topped with a suite of partially resolved hopanes (Figures 5 and 6). These hopanes are considered to be good identifiers of "Amoco Cadiz" oil (Boehm, 1982), and are persistent. For concentrations typical of the samples received, the Lagomedio from BIOS would still have significant resolved alkanes and less UCM. The type of weathering which resulted in the "Amoco Cadiz" stage 4 weathering must include significant biodegradation. The two samples of the "latex" oil from Aber Benoit and Croix (Figure 6) show similar weathering to the other samples from the marsh (Figure 5a) and from the asphalt pavements (Figures 5b, 5c, and 5d).

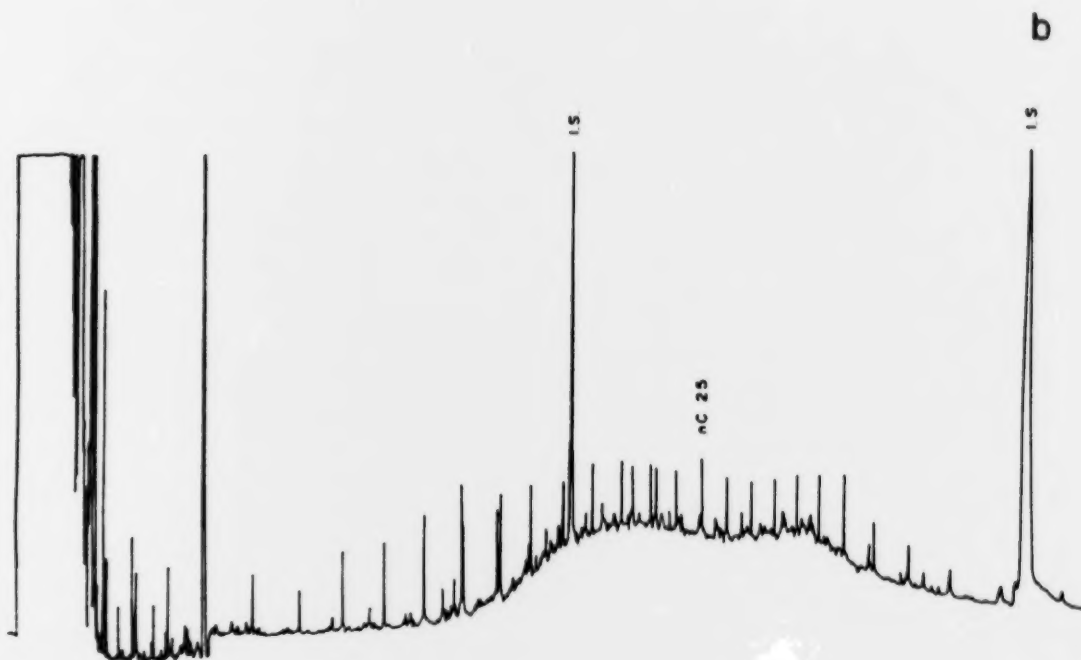


Figure 2. Surface(a) and subsurface(b) samples:
GC traces from backshore crude oil
plot (T1), Cape Hatt. Oil "spilled"
20 August 1980; samples collected
11 August 1985.

Figure 3. Surface(a) and subsurface(b) samples:
GC traces from intertidal asphalt
pavement, Bay 11, Cape Hatt. Oil
stranded on 19 August 1981; samples
collected 9 August 1985.



5054: Bay 11, Profile 4 Upper Surface



5056: Bay 11, Profile 4 Lower Surface

Figure 4. GC traces from (a) upper intertidal and (b) lower intertidal zone surface samples collected from asphalt pavement on Bay 11, at Cape Hatt, N.W.T. Oil stranded on 19 August 1981; samples collected on 9 August 1985.

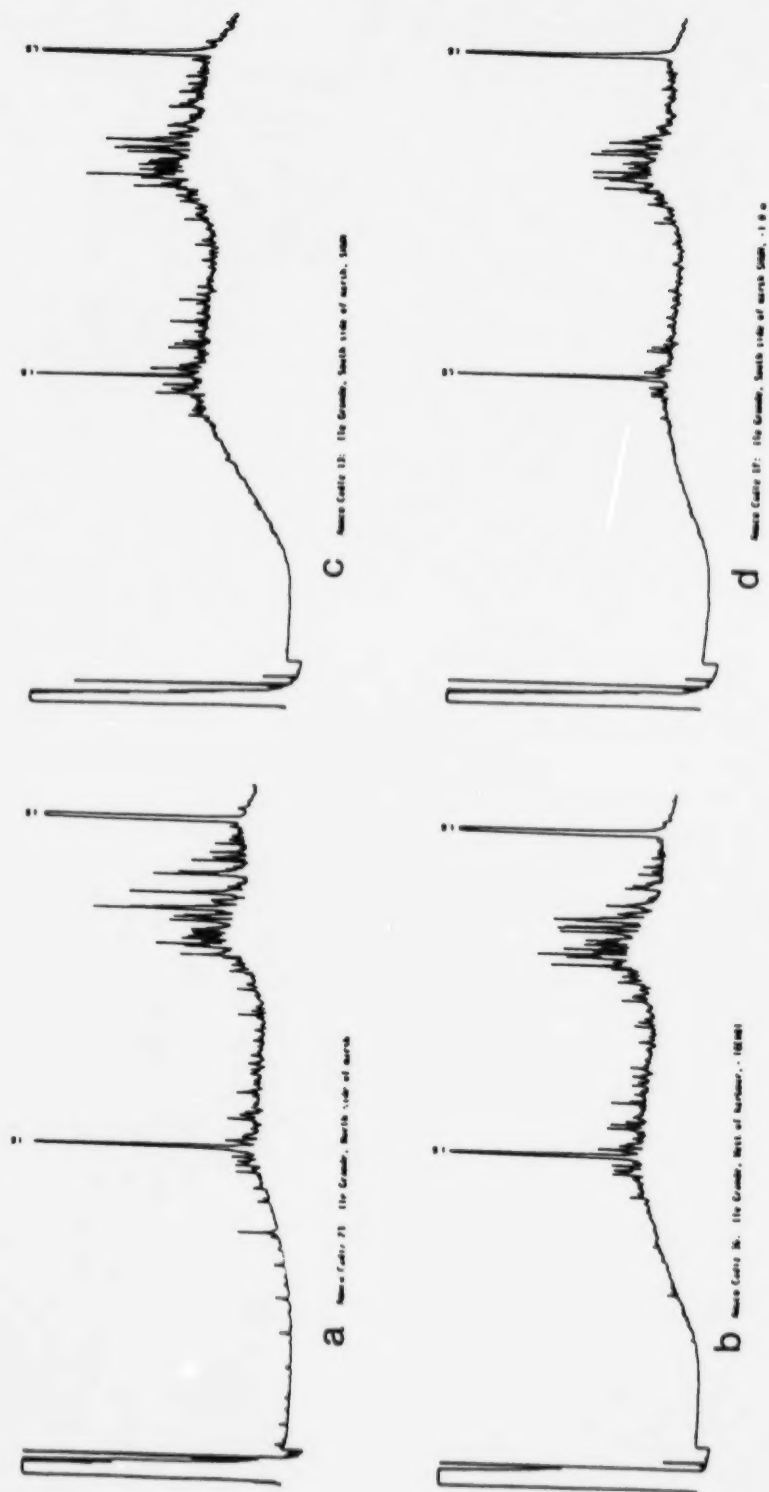


Figure 5. GC traces from the Ile Grande area. "Amoco Cadiz" oil spilled March/April 1978, samples collected March 1985 (Owens and Robson, 1985; Hope and Humphrey, 1986).

- (a) marsh surface - Ile Grande: sand-mud sediments
- (b) asphalt pavement near SHWM - Toenot
- (c) asphalt pavement at SHWM - Toenot
- (d) asphalt pavement below SHWM - Ile Grande

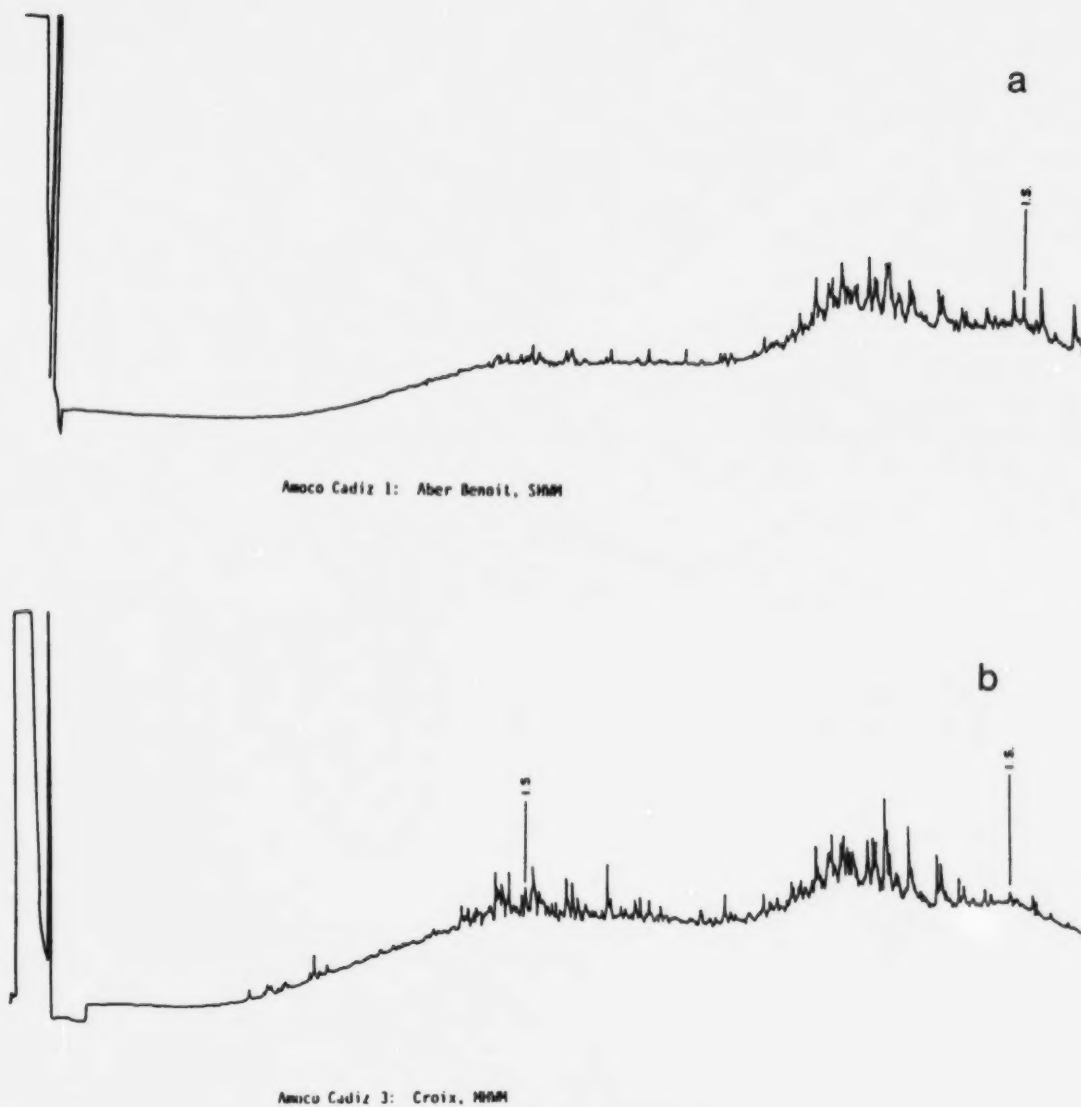


Figure 6. GC traces from surface "latex" mats. Oil stranded March/April 1978, samples collected March 1985 (Owens and Robson, 1985; Hope and Humphrey, 1986).
(a) Aber Benoit, near SHWM
(b) Croix, near MHWM

DISCUSSION

(a) The Character and Formation of Asphalt Pavements

The observations and data reported above, as well as earlier discussions (Owens 1971, 1978), provide a reasonably consistent picture of the character of asphalt pavements. The definition provided at the beginning of this paper can be expanded by considering the conditions under which an asphalt pavement is likely to form. Intertidal pavements have been observed to develop (1) either in the zone between the mean high water mark (MHW) and the spring high water mark (SHW) or on the low-tide terrace, (2) on well-drained substrates, not finer than medium-grain sand, (3) which have a low angle of inclination, (4) which are protected by some means or mechanism from strong physical forces, (5) which do not exhibit a high ground-water table, and (6) where sufficient time permits penetration and weathering of the stranded oil. Taking each of these points in more detail:

(1) Oil laid down above the MHW may only be covered by water during high tides on 10 or 15 occasions each month. This inundation depends upon the width of the beach and the tidal range. Any oil in this zone is, therefore, not as exposed to the eroding effects of water washing over the surface as oil that is stranded below the MHW. By contrast, pavements may form in the lower intertidal zone, which is inundated during most of the tidal cycle. On low-tide terraces, where a coarse-sediment deposit is present and which are well-drained, oil can accumulate during the low-tide slack period. If the oil is not refloated by the flooding tide a pavement could eventually develop.

(2) The pavements are well anchored into the beach. Well-drained sediments, which are permeable, allow viscous oils to penetrate the upper layer of beach sediments and thereby become incorporated into the sediment. Initially the surface oil that had not penetrated the sediments would serve to protect the developing pavement mixture. As the surface oil is removed the emerging asphalt pavement would be more resistant to erosion and weathering. If the sediments are too fine or the oil too viscous, thus preventing penetration, then the oil could be more easily removed even by infrequent or low-energy tidal or wave forces. A pavement can only form on a sand beach if the oil can penetrate into the surface sediments, whereas on a pebble beach virtually all oils can migrate through interstitial spaces. In the latter case an oil must have some internal cohesion or it will migrate below the surface and an insufficient volume will remain on the surface to form a pavement.

(3) The angle of inclination of the beach or beach face will affect the residence time of oil on the surface and hence the potential for oil penetration. More oil would likely penetrate and remain in the surface sediments on low- versus high-angle sections of a beach. Also water tends to run quicker over steeper surfaces, which would result in more energetic physical forces coming in contact with stranded oil.

(4) One of the most important components in creating the time for the pavement to form is protection from high-energy forces. Wide, gently sloping beaches that limit wave height on the beach face or physical obstacles that reduce fetch both tend to increase the time that the oil remains on the sediments, which in turn increases penetration potential and subsequently surface weathering.

(5) High ground-water tables would act as a barrier to oil penetration of beach sediments and in extreme cases, if the surface sediments are wet, this would reduce the opportunity for oil to remain and penetrate.

(6) Finally, sufficient time must elapse after the oil becomes stranded to allow oil to penetrate into the surface layer of the beach sediments and to weather the exposed surface oil.

Physically, asphalt pavements vary in thickness between 5 and 20 cm and are usually only eroded along the edges. They may be buried during an accretional stage or undercut by erosional action. They can persist for periods in excess of 10 years: remnants of asphalt pavements that resulted from the "Arrow" spill in Chedabucto Bay, Nova Scotia in 1970 were observed as recently as 1982 (by E.H.O.) and 1985 (by J.Vandermeulen). Data on oil from these pavements are presented elsewhere in this volume by Vandermeulen and Humphrey. Surveys of the "Metula" and BIOS sites, 6½ and 4 years respectively after the spills, show that extensive pavements can persist for at least these time periods. The "Amoco Cadiz" and "Arrow" observations, 7 and 15 years respectively after the spill, showed in these instances that fragments of pavement, some on the order of 50 m², had persisted. In the "Amoco Cadiz" case large areas of "latex" mat persisted at several locations.

It is not possible to predict the expected persistence time of an asphalt pavement. Once formed, it is erosion resistant and may persist for 5, 10 or even more years.

An oil mat was observed at several sheltered mud flat and marsh locations near Croix and Ile Grande during the "Amoco Cadiz" site visits. This mat was coincident with fine-grained sediments and, unlike a pavement, was not mixed with sediment. Although extensive in area, this mat often was not immediately obvious from a distance due to vegetation growth through the oil cover. This mat, or "latex-type" cover, is different from a pavement as the oil rested on the sediment surface and contained little or no incorporated sediments. This mat was found to occur only with fine-grained (i.e. closely packed) sediments and it is likely that the same oil type may form a mat cover on fine sediments and an asphalt pavement on coarse sediments (Owens and Robson, 1985).

(b) Total Hydrocarbon Data and GC Results

A summary of the total hydrocarbon data (Table 6) provides a comparable data set from 3 separate studies. The trends of decreasing concentrations through time may not be real due to differences between the study areas. The BIOS data set provides a time-series that shows a decrease in concentrations on the backshore control plot (Table 7a) but a strong consistency through time in the samples taken from the beach-face area of Bay 11 (Table 7b). This latter point is considered realistic as concentrations in a stable feature such as an asphalt pavement would not be expected to change significantly through time if the physical character of the pavement is unchanged. The GC results show that little weathering has occurred since 1981 on the backshore plot so that the reduction in oil concentrations from this data set is unexplained at this time.

Table 6. Summary of Asphalt Pavement Oil Concentrations

	MONTHS AFTER SPILL	BEACH-FACE OIL CONCENTRATIONS (mg/kg)		LOW-TIDE TERRACE OIL CONCENTRATIONS (mg/kg)	
		Mean	Range	Mean	Range
"Metula"	32	47,350	8,000-82,000	18,400	2,600-33,000
BIOS intertidal	48*	19,000	12,000-25,000	11,600	4,000-24,000
"Amoco Cadiz"	84	9,300	5,000-16,000	—	—
BIOS backshore	60	16,000	13,000-20,000	—	—

* Equivalent to 12 Open-Water Months

Table 7. BIOS Total Hydrocarbon Data from Backshore and Intertidal Locations, 1980-1985

YEAR	MONTHS AFTER "SPILL"	OIL-IN-SEDIMENT CONCENTRATION (mg/kg)
(a) Backshore Control Plot T1		
1980	0	58,000
1981	12	31,000
1982	24	28,500
1983	36	9,000
1985	60	16,000
(b) Intertidal (Beach-Face Pavement) - Bay 11		
1981	0 (0)*	17,000
1982	12 (3)	12,300
1983	24 (6)	19,800
1985	48 (12)	19,000

* Equivalent open-water months

The differences in oil concentrations between locations are considered to be a function of loading (Owens and Robson, 1986). The maximum loading of the BIOS beaches ranged from 10,000 to 60,000 mg/kg. Higher loadings would be expected in areas where fine-grained sediments (i.e. sand) were less predominant, as these fill much of the interstitial spaces on mixed pebble-sand beaches. This is probably the case in the "Metula" data set as the beach sediments in several of the pavement sections of that area are better sorted and contain a higher pebble fraction when compared to the Cape Hatt beaches. The Punta Espora site has sediments very similar in size and sorting to the Cape Hatt Bay 11 location and has similar oil concentrations (22,000 and 19,000 mg/kg respectively).

The trend of lower oil concentration values on low-tide terrace pavements as compared to higher values on beach-face pavements is considered real. The intertidal zone is both inundated and effected by wave processes for longer time periods than the upper intertidal zone. This is particularly important prior to stabilisation or "asphaltization" of the oil, as more oil is likely to be removed from the lower beach areas. In both the "Metula" and BIOS areas the low-tide terrace pavements cover considerably smaller areas than the beach-face pavements. In the BIOS Bay 11 area, the latter accounts for over 75% of the total pavement area.

The GC results show that the BIOS samples from the lower intertidal zone were more weathered than those from the upper beach and backshore locations. The evaporative weathering occurred primarily within one year (1980-1981). The data also shows that where the oil remains in high concentrations, as is common in a pavement, the SHW and ALK/ISO ratios remain higher, indicating lower weathering rates when compared to samples with lower oil concentrations.

ACKNOWLEDGEMENTS

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SHORT-TERM OIL SPILL TRANSPORT MODEL

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INTRODUCTION

The focus of the U.S. Coast Guard's Arctic Spill Response project is to insure that the On-Scene Coordinator (OSC) has the background information and technical expertise to monitor the progress of an Arctic oil spill and its cleanup operation. Initially, it may be crucial for the OSC to determine pertinent facts about a particular discharge of oil particularly the probable direction and speed of advance of the oil. This will provide him with the information to make judgements concerning the areas where the environment will be affected, and the resources and priorities for protecting them. Should a spill occur today, the best method for forecasting during the early stage of the spill would be similar to the basic vector addition technique used by the National Response Center for many past spills. This technique is excellent for immediate forecasts of the oil slick's directional movement and outer boundaries. The vector technique has been incorporated into a simple computer model designed for Arctic areas. The information provided by the model using the vector addition technique will be the fundamental source for information for the OSC until the National Oceanographic and Atmospheric Administration (NOAA) Scientific Support Coordinator (SSC) can be activated.

The oil spill model that has been developed is easily accessible and, most important, easy to implement. It is designed so that on being notified of a spill the OSC can turn the computer on, feed in a small amount of easily obtained data and then let the computer run while the OSC is preparing to respond to the scene of the spill. When ready to depart the OSC will return to the computer and gather the printed output. Thus, for the OSC, a forecasting system has been developed which will:

- a. Predict the movement of the oil spill with sufficient accuracy to permit the OSC to make proper decisions about the deployment of his resources.
- b. Consider all factors affecting the movement of the oil slick including: spreading, size and time of original discharge, size and time of any additional discharges, winds, surface currents, and site-specific geography.
- c. Require as inputs only that information which is readily available to the OSC such as: time and size of spill, location of spill and local weather conditions.
- d. Be capable of providing updated projections as additional information becomes available or conditions change.
- e. Be capable of real-time operation to give timely results.
- f. Present its output in a format that can be easily used and understood.

A shortcoming of many models occurs not in the development stage of the algorithms but in the validation of these models to real-world events that they are trying to predict. Therefore, it was considered essential that the short-term predictive model be tested to determine its ability to provide the basic parameters of oil slick directional movement and outer boundaries.

COMPUTER MODEL

In the model the movement of a waterborne conservative property such as an oil slick is assumed to be described by a diffusion-advection equation. The equation describes the Eulerian concept of concentration changes with time at fixed locations as the oil is advected and diffused over a region. The diffusion equation was tested in zero current fields. Coefficients were determined for this equation which allowed for a circular spread rate comparable to those rates determined from actual spills and laboratory experiments.

The advective portion of the equation is considered to be the most important part of the model. The advective equation is a fourth-order computational scheme based on work performed by Crowley (1968). Using these equations allows conservation of oil quantities as well as permitting concentrations to be affected by the converging and diverging current pattern systems that are input to the equations.

SURFACE CURRENTS

The area of the Beaufort Sea shelf for which the model was developed is that portion landward of the 40 meter isobath. Current measurements in this area are sparse due to the difficulty of setting and maintaining current meter moorings in the presence of sea ice. However, drifter data, from Matthews (1981), and current meter measurements made by Aagaard (1981) provide some information about the surface water movement. Generally these studies indicate that the water movement on the shelf tends to be in the longshelf direction (generally east and west). However, there is an occasional cross-shelf flow (north and south) of a highly variable nature. It has been generally agreed that the predominant mechanism for water movement on the inner shelf and within the barrier islands is the wind. This hypothesis is supported by several different researchers including Lissauer and Matthews (1982), Matthews (1979), Mungall and Whitaker (1979) and Barnes and Reimnitz (1977). Lissauer and Matthews (1982) studied the movement of surface drifters placed under the shorefast ice just prior to summer break-up of ice and in leads in the pack ice on the inner shelf. Results of the drifter returns from two years of releases show 74% were found to the west of their release points indicating a predominant westerly flow. This westerly flow is in agreement with the dominance of easterly winds in the area of the drifter releases documented by Hufford, et al., (1976). Barnes and Reimnitz (1977) has reported good correlations between near surface currents and local winds off of Prudhoe Bay, Alaska.

A key ingredient to the successful implementation of the model was the development of the current data base for input to the model. In 1979 the Coast Guard R&D Center conducted an experiment to observe the dynamics of ice movement during break-up of the ice in the Prudhoe Bay area (Lissauer and Tebeau, 1980).

During surveys conducted with ice concentrations of less than 50%, floe speed varied between 6.0% and 11.7% of the wind speed for one survey and 5.5% and 12.4% for the second survey. These values are significant because they greatly exceed the expected 2-3% values commonly referred to in the literature. Generally, for oil spill models a wind factor of 3.5% is used with the other forces that tend to move the oil.

Lissauer, et al., 1984, examined the circulation on the Beaufort Sea Shelf in "Atlas of the Beaufort Sea." As noted before it was determined that the

Beaufort coastline is dominated by a long-shore transport caused by large-scale meteorological conditions. Persistent winds from the northeast or strong northwest winds cause patterns of mean current conditions. An example of these patterns is shown in Figure 1. This pattern is based on a northeast wind of ten knots. There is a formula within the Atlas to rescale these values for lower or higher wind speeds. In order to determine the transport of oil a simple vector technique is presented in the Atlas. This transport is determined by adding 3% of the wind speed to the mean currents shown in Figure 1. Thus for a local northeast wind of ten knots in the vicinity of Prudhoe Bay oil would be transported by the mean currents (which are approximately 3% of the wind) and an additional 3% factor for the local wind. Thus oil transport could be approximately 6% if the mean currents and the local wind transport were in the same direction. Such values would be similar to those collected during the ice dynamics experiment previously discussed.

FIELD EXPERIMENT

The field experiment was designed to obtain surface current measurements for comparison with the data base of surface currents, and to test the short-term model. Surface current measurements were recorded at several locations. Figure 2 is an example of one of the recordings of these measurements. Twenty-one such measurements were made. The average speed was computed for each recording and compared to 3% of the average wind speed for the period of the recording. If oil were moved solely by the local wind then the current speeds should approximate the 3% wind speed values. However, as discussed before the current speeds should exceed the 3% value of the wind speed because of the addition of the mean current to the local wind current. This is clearly demonstrated in Figure 3 where the measured current speed values exceed the wind values in all but three cases. The three values where the wind speed exceeded the current speed were all measured in 80-90% ice coverage near the edge of the pack ice. Thus the ice tended to impede the local wind drift as well as the mean currents caused by the large-scale meteorological conditions.

Once the validity of the data base was determined it was necessary to validate the model. Tests were conducted during the period 1-14 August 1985 in the area north of Prudhoe Bay. A microwave tracking system (MTS) was set up at Prudhoe Bay. Transponders for the system were placed at east dock, west dock, and on Cross Island. The MTS system can track transponders at line-of-sight distances. The Center has developed surface drifters with transponders imbedded in them. The drifters consist of a waterproof box floated by polystyrene foam sandwiched between two pieces of plexiglass. An MTS transponder and batteries are contained in the waterproof box and are connected by flexible wave guides to the antenna on a 4-foot pole. The drifters float with the upper surface awash, thus the leeway of the drifter is expected to be small to negligible. The structure of the drifter is such that it marks the movement of the upper 2 to 3 feet of water, which is deeper than the layer that will affect an oil spill. The MTS drifters were tested for their ability to describe leeway movement by deploying one or more drift cards next to them. The drift cards were brightly painted 4 feet by 4 feet sheets of 1/2-inch plywood whose positions were marked periodically by a monitor boat. Although the absolute motion of the MTS drifters and the drift cards was very similar, some relative motion was observed. In light winds, calm conditions, the drift cards had a greater motion downwind than the drifter. In 14-20 knot winds, there was no appreciable difference in their motion.

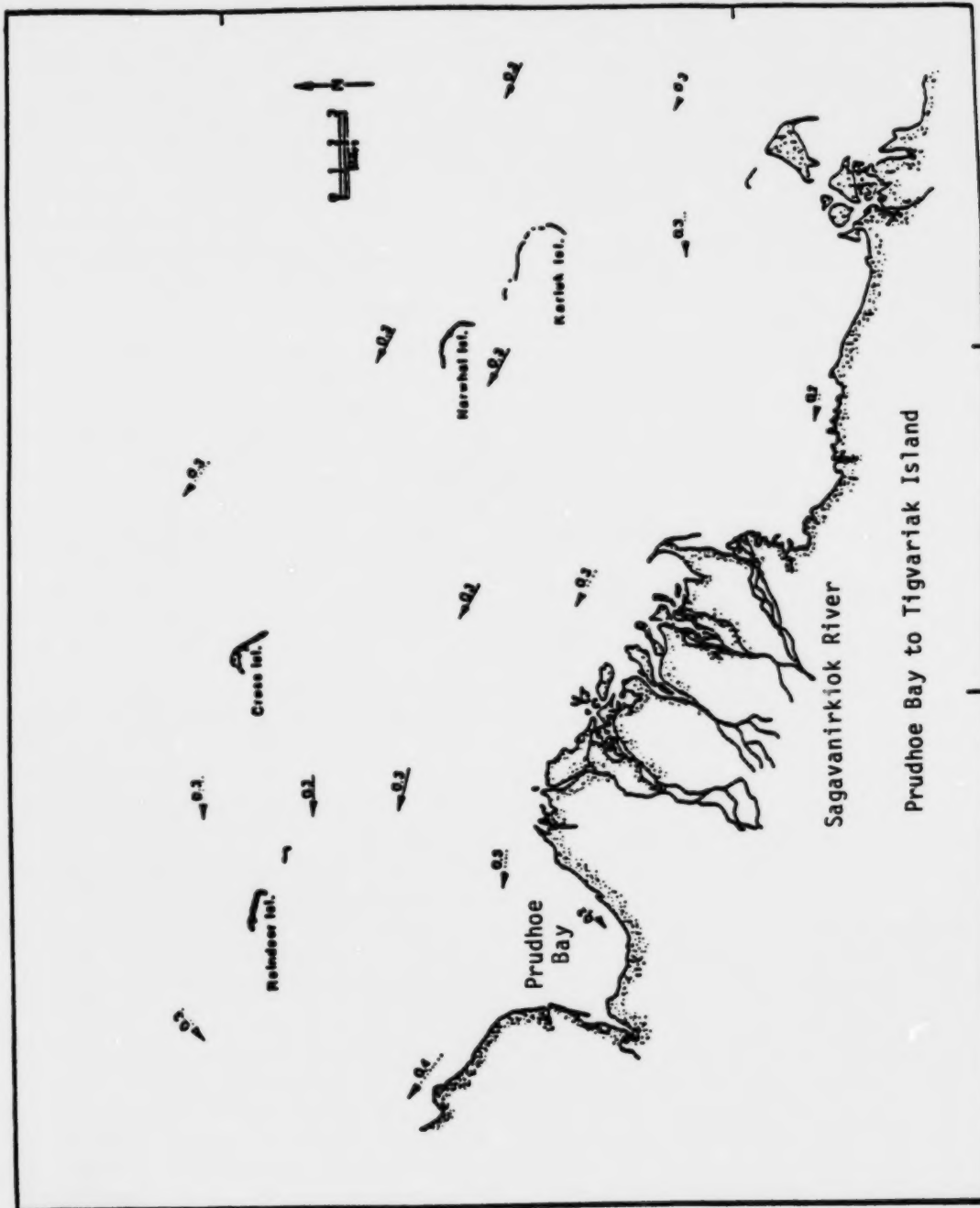


FIGURE 1 - MEAN CURRENTS IN THE VICINITY OF PRUDHOE BAY FOR A NORTHEAST WIND AT 10 KNOTS

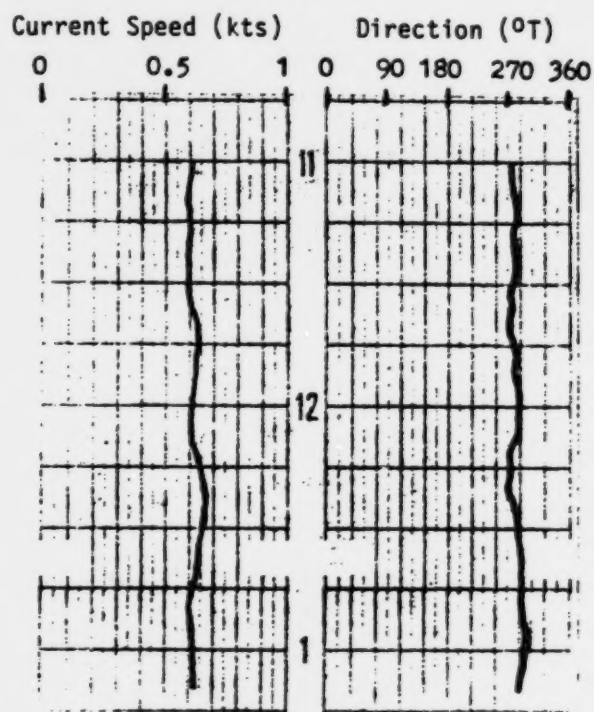


FIGURE 2 - SAMPLE OF RECORDED CURRENT SPEED AND DIRECTION

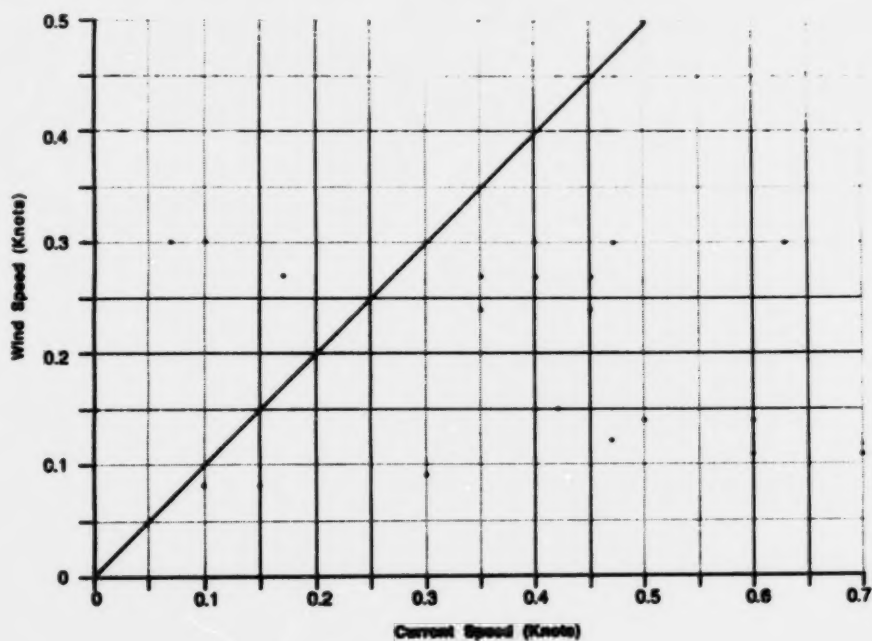


FIGURE 3 - COMPARISON OF CURRENT SPEEDS WITH 3% VALUES OF THE WIND SPEED

This may be due to light winds only moving the top few inches of the water; while in rough sea, turbulence smooths out the vertical gradient of current for the upper few feet. Therefore, the effect of the surface current on an oil spill may be somewhat different than the effect on the drifters in light winds. However, because of errors caused by estimations of winds and their variability, this difference will not cause a significant problem for the validation of the model.

Figure 4 illustrates a drift track that was obtained. The small circle indicates the start of the drift path and the capital letter marks the drifter location when it was removed from the water. The letter S indicates one of the tracking system stations, and the letter B at the bottom of the page indicates the location of our command post where the computers were receiving drift data.

In order to verify the predictive capability of the model, the drift tracks were overlaid on model outputs. Figure 5 shows the model output and drift tracks. The model displays letters (H, M, L) which correspond to oil concentrations of High, Medium or Low, which are relative terms. The path of the drifters is shown by an arrow with the starting point of the drift marked by a circle. The shoreline and barrier islands are represented by the dotted figures. Reindeer Island is shown north of the drift track and Cross Island is shown to the lower right of the drift track.

This first drift period on 4 August 1985 lasted for just under seven hours. The comparison of the drift track to the model output is in good agreement. The core of the oil spill simulation for the model output appears to be slightly to the south of the drift track, and the drift track exceeded the model output distance by approximately one grid square (1413 meters). However, for the objective of the model to provide the general direction of movement and approximate rate of advance of the oil, the results exceeded our expectations of the forecasting ability of the model.

The other model outputs for the various drifts were in excellent agreement with the drift tracks. These drift data indicate the ability of the model to successfully simulate the direction of movement and speed of advance of an oil spill in the Arctic. It will provide the OSC with an adequate prediction technique for the short-term period of 24 hours.



FIGURE 4 - DRIFT RUN #1, 4 AUGUST 1985



FIGURE 5 - COMPARISON OF MODEL OUTPUT TO THE PATH OF
 MOVEMENT OF DRIFT RUN #1, 4 AUGUST 1985

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THE CHARACTERIZATION OF FIFTEEN YEAR OLD STRANDED OIL

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INTRODUCTION

Marine transportation of petroleum hydrocarbons provides the possibility that the hydrocarbons will be spilled on the sea. For two types of material, crude oil and bunker fuels, there is a good possibility that some portion of the oil will be resistant to removal by natural means such as evaporation or biodegradation. These residues, if on shorelines or in sediments, may be persistent and have an effect on the local environment for a long period of time. While short term effects are often monitored, it is rare that the long term effects are studied. The composition of freshly spilled oil can be determined by standard analytical methods, but little is known of the chemical character of the residual oil.

There are many sites in the world, and a few in Canada, where spilled oil remains on a beach or in a marsh many years after the spill. In some cases the oil is left in place for monitoring purposes (eg Irish Stardust, Cretney *et al*, 1974), to test countermeasure techniques (eg Golden Robin, Vandermeulen and Ross, 1977), as part of an experimental oil spill (eg the BIOS experiment, Sergy and Blackhall, 1986) or is left behind after cleanup operations cease (eg Amoco Cadiz, Owens and Robson, 1985). One particular example is the area of the Janvrin Lagoon in Chedabucto Bay, the site of the Arrow spill in 1970. These stranded oils present special environmental problems in that they are in low energy environments, often persisting for decades after their initial deposition.

Recent observations at the site of the Arrow Bunker C spill show residual tars in a number of locations on shorelines, as well as Bunker C derived hydrocarbons within the intertidal sediments of those beaches. These observations are similar to those made at Cape Hatt, the site of the BIOS experiments (Owens *et al*, 1986) and in various locations on the coast of Brittany, where oil from the Amoco Cadiz has been observed and some samples analysed. (Owens and Robson, 1985; Owens *et al*, 1986).

These stranded oils are usually very weathered, having lost by evaporation or dissolution most of the lower molecular weight components known to be toxic. However, the persistence of stranded oils in the environment may generate a long-term environmental problem because of the continued availability of less toxic material.

In addition, photochemical and microbiological weathering may be modifying the oil components, potentially producing more toxic and more available compounds.

Crude oil consists of a large portion of alkane and alkene hydrocarbons, and lesser portions of aromatic and substituted hydrocarbons. During refining processes and during weathering in the environment, the low molecular weight alkane, alkene and aromatic fractions are removed, leaving high molecular weight and polar materials behind.

Very weathered oils present considerable analytical problems. The common techniques for characterizing oils examine the major components, the low molecular weight materials which are of greatest commercial value. Few techniques are available to analyse for or characterize the high molecular weight materials or the polar materials. We have been interested in the characterization of these stranded oils in order to estimate their long-term impact on benthic biota. The techniques we have selected include those used by the heavy oil and shale oil industries.

We have analysed samples collected from Janvrin Lagoon in Chedabucto Bay in October, 1985, more than fifteen years after the spill; an original sample from the Arrow; and a sample of sediment from Potatoe Island, in Chedabucto Bay, as a control. The Janvrin Lagoon samples are from the upper intertidal pavement like area, and from two intertidal sediments, one heavily oiled and one lightly oiled. We have also compared some of the results to Kuwait cude oil.

METHODOLOGY

Samples were collected from the Janvrin Lagoon area and Potatoe Island on October 31, 1985. The samples were placed in glass jars and kept frozen until analysis, which occurred over the next two weeks.

Our approach has been to separate the stranded oil into chemical class fractions, using a column chromatography scheme based on those of Schiller and Mathiason (1977) and Later et al (1981). This procedure was selected as it separates the hydrocarbon materials into the fractions of greatest interest to us, is simple, and provides fractions in a solvent suitable for further high performance liquid chromatography (HPLC) analysis. The whole oil and the chemical class fractions were further fractionated using a molecular weight discriminating HPLC technique similar to that of Dark (1978).

Each sediment sample was extracted with tetrahydrofuran (THF) on a shaker. The combined THF fractions were filtered and reduced in volume to either 25 mL or 5 mL. For subsequent fractionation, a known volume of the solution was added to dry alumina and evaporated on a rotary evaporator to produce a slurry.

The fractionation is carried out by placing the slurry of the oil in alumina on top of a column of 6 g alumina slurry packed with hexane. The column was then eluted successively with 20 mL hexane (F1- aliphatic hydrocarbons), 50 mL benzene (F2- neutral polycyclic aromatic hydrocarbons (PAH)), 70 mL chloroform with 0.75% ethanol (F3- nitrogen substituted PAH), and 50 mL THF/ethanol 9:1 (F4- amino PAH). Each fraction was evaporated on a rotary evaporator and the solvent exchanged twice for THF, and the final solution diluted to 5 mL in a volumetric flask. A gravimetric determination was made of each fraction.

The F2, F3, and F4 fractions obtained from the column chromatography were analysed for molecular weight distribution using gel permeation HPLC. Fraction 1 from each was not analysed as the detector used could not respond to an alkane fraction.

The HPLC analysis was carried out using a Spectra Physics Model 3500B HPLC fitted with two uStyragel 500Å and one uStyragel 100Å gel permeation columns (Waters & Associates) in series. This column set up is designed to separate compounds of molecular weight 100 to 10,000. Standard molecular weight materials were used to calibrate the separations. The solvent used was THF, and the detector used was a fluorescence detector, set for excitation at 240 nm and emission at 410 nm.

The hydrocarbon content of each extracted oil sample and the column fractions from the Arrow oil and Janvrin Lagoon pavement was determined by evaporating a measured volume of each solution on a tared weighing boat.

The composition of each column fraction was determined by gas chromatography using a Hewlett-Packard 5730A gas chromatograph with a fused silica DB5-15N 0.25 mm capillary column. The temperature was programed for a 4 min 90°C isothermal period, followed by a ramp of 8°C min⁻¹ to 250°C, then a 16 min. isothermal period. The detector was a flame ionization detector (FID)

The whole oil extracts in THF and the fractions, also in THF, were analysed by synchronous scan fluorometry, based on the method of Lloyd (1971). Using a Perkin-Elmer MPF 3L Spectrofluorometer, each solution was scanned from an excitation wavelength of 200 nm to 530 nm, with a wavelength difference of 23 nm.

The solutions were evaporated on a sodium chloride plate and scanned from 4000 cm⁻¹ to 800 cm⁻¹ using a Perkin Elmer 337 Infra-red spectrophotometer.

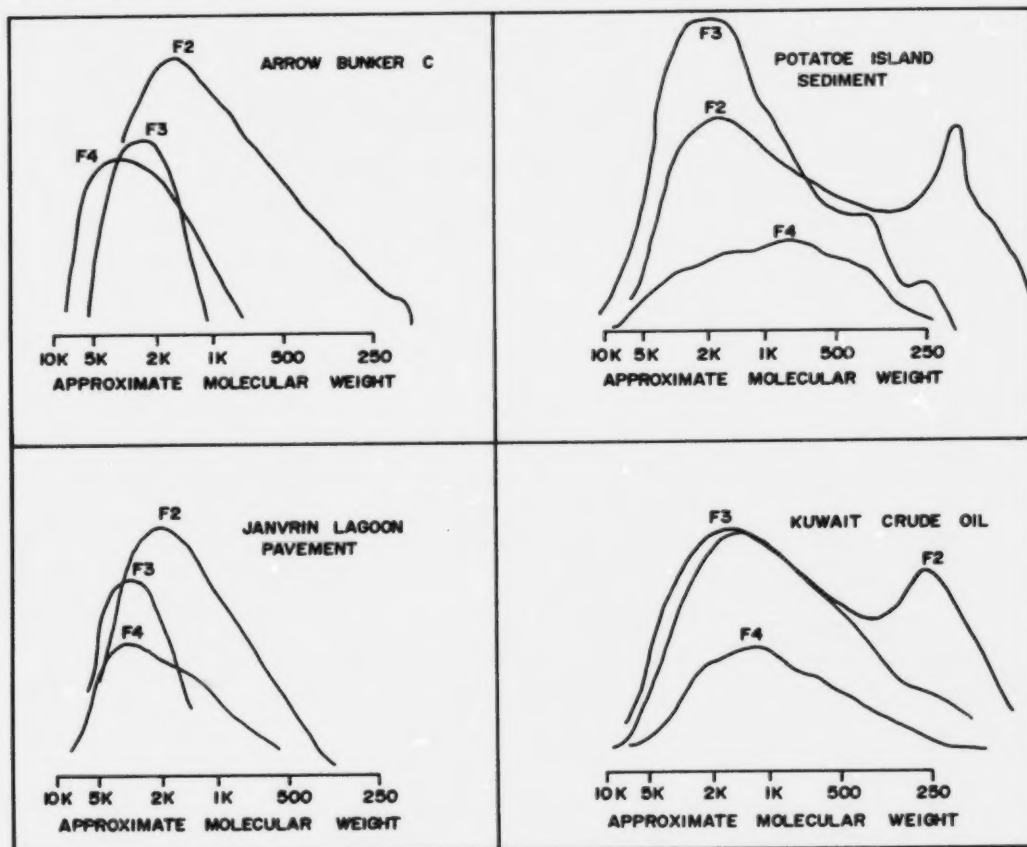


Figure 1

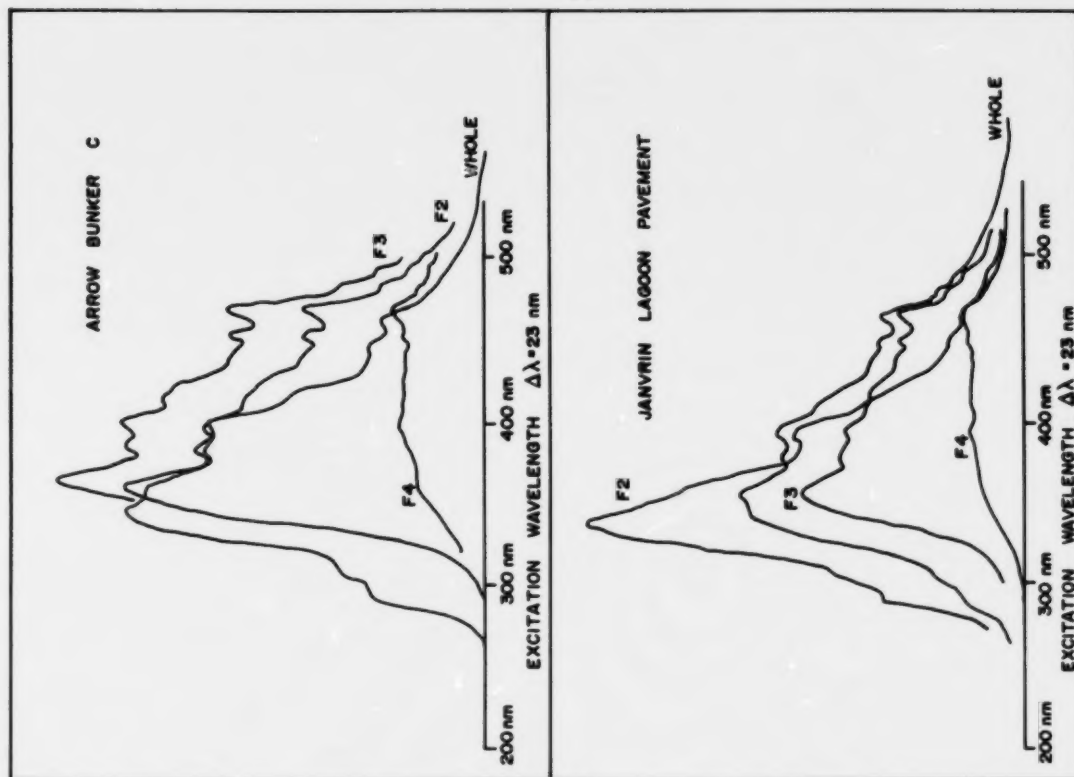


Figure 3

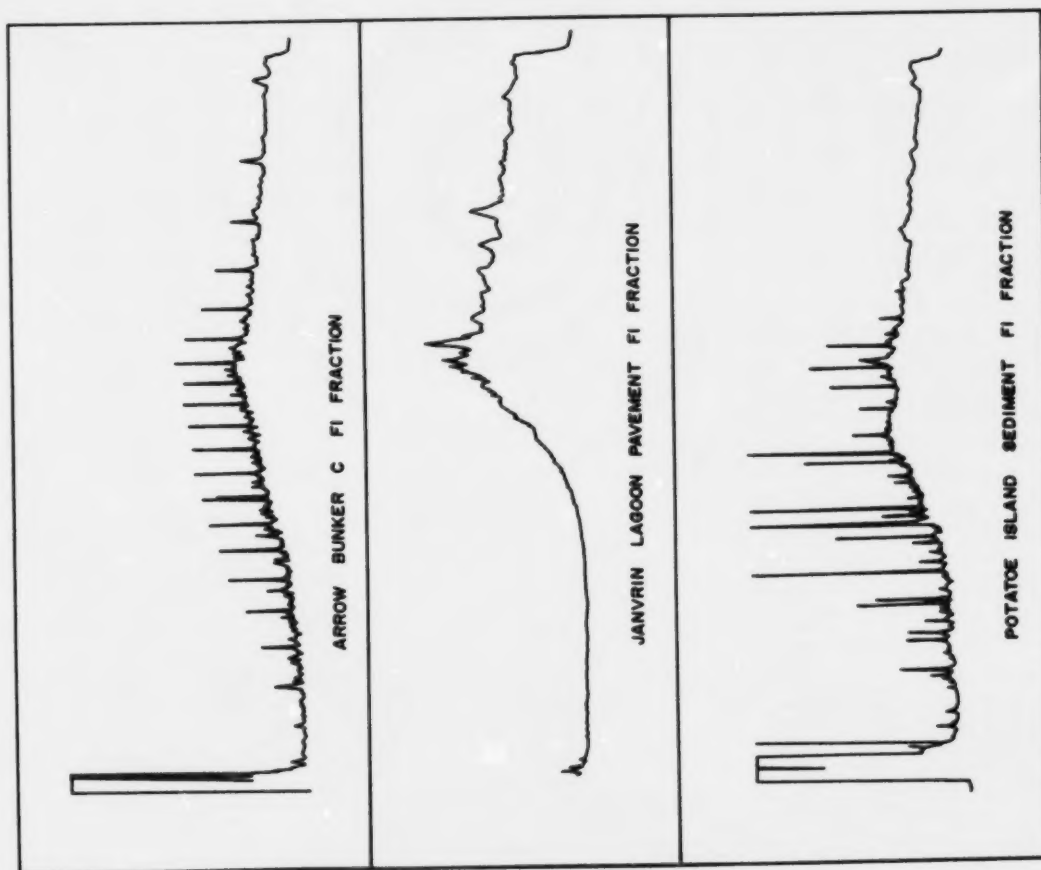


Figure 2

RESULTS

The column chromatography separation of all samples resulted in visible amounts of each component. The samples from the Arrow and from the Janvrin Lagoon pavement were in quantities suitable for microgravimetric analysis. The other sediment fractions and the Potatoe Island control fractions were not suitable for microgravimetric analysis, as the balance precision could not distinguish the tared weigh boat from the boat plus fraction. The oil content and fraction composition of each sample is listed in Table 1.

Table 1

Sample	Hydrocarbon Content	% composition				% Recovered
		F1	F2	F3	F4	
Arrow Bunker C	Pure	20	13	10	56	56
Janvrin L. Pavement	11%	11	8	34	47	96
Janvrin Sediment 1	0.7%	Not Determined				
Janvrin Sediment 2	0.07%	Not Determined				
Potatoe Island	0.04%	Not Determined				

The results of molecular weight analyses of the fractions obtained from the columns are presented for the Arrow Bunker C, the Janvrin Lagoon pavement, Potatoe Island sediment, and Kuwait crude oil. Figure 1 shows the chromatogram maxima for the three analysed fractions. No scale is presented for the abscissa as no response factors for the fluorescent detector have been determined. The plots should be accepted as qualitative only at this time. The results for the Janvrin sediments 1 and 2 are indistinguishable in shape from the Janvrin Lagoon pavement chromatogram.

A comparison between the original Arrow oil and the fifteen year old pavement material indicates a strong similarity in molecular weight distribution, except that the lower molecular weight components of the F2 (PAH) are depleted in the stranded oil. The molecular weight distribution of the Potatoe Island fractions are quite different, with generally lower molecular weight distributions for the F2 and F4 fractions. For comparison, the distribution for the Kuwait crude, a light crude oil, again indicated a higher proportion of lower molecular weight material.

Gas chromatograms were obtained for each of the four fractions for all samples. Figure 2 presents the chromatograms for the F1 fractions of the Arrow oil, the Janvrin Lagoon pavement, and Potatoe Island sediment. The Bunker C chromatogram is essentially the same as that reported elsewhere (Keizer et al, 1978). The Janvrin Lagoon pavement chromatogram is typical of very heavily weathered oil, with only unresolved complex mixture present. The chromatograms of weathered oil reported by Keizer et al (1978), which had been sampled in 1976, five years after the spill, did not indicate as much weathering, with many resolved alkanes present in the higher concentration samples. The Potatoe Island sediment F1 fraction is typical of naturally occurring hydrocarbons, with some resolved but unidentified substituted alkanes and an odd-even predominance indicated for the n-alkanes observed.

The F2 fraction chromatograms indicate similar conditions: the Arrow Bunker C contains resolvable components, the Janvrin Lagoon pavement does not, and the Potatoe Island sediment contains resolvable components, although those components are not the same as those in the Arrow Bunker C chromatogram. The F3 and F4 fractions did not contain resolvable components for either the Arrow Bunker C or the Janvrin Lagoon pavement, although the F3 and F4 fractions of the Potatoe Island sediment did include resolvable low molecular weight material.

Chromatograms of the low concentration sediments from the Janvrin area included unresolved complex mixture overlaid with some resolvable components typical of the natural components as observed in the Potatoe Island sediments.

The synchronous scan fluorescence spectra for the whole extract and the F2, F3, and F4 fractions of the Arrow Bunker C and Janvrin Lagoon pavement are presented in Figure 3. The whole extract spectrum for the Arrow oil indicates the broad response typical of a mixture of aromatic ring systems. The fractionation process appears to remove some small ring components as indicated by the loss of the emissions around 300 nm. With each succeeding fraction, the shift to higher emission wavelengths implies that the proportion of higher ring number components is increasing, with the F4 being composed of five and more rings.

Similar results are found for the Janvrin Lagoon pavement. The F2 fraction appears to have an increase in the proportion of lower ring number aromatics than in the original oil, but the other fractions are very close to those of the Arrow oil. The whole extract spectrum indicates a slightly lower content of small ring aromatics.

The infra-red spectra of all samples do not contain any absorbances which may be assigned to functional groups other than CH and substituted aromatics.

DISCUSSION

The common methodology for the analysis of environmental samples for petroleum hydrocarbons is based on an extraction and subsequent determination of the alkane components by GC and sometimes determination of a selected number of aromatic compounds by GC/MS. In some cases, a screening of samples for petroleum hydrocarbons is done, using synchronous scan fluorescence (eg, Boehm et al, 1985). Normally, this method requires knowledge of the potential contaminant, as was possible in the case of the BIOS experiments. Both GC and GC/MS methods examine the lower molecular weight components of the petroleum hydrocarbon, and the information obtained has been interpreted in those terms. When oil becomes weathered, those specific components are often no longer present, and data interpretation becomes more difficult. The synchronous scan fluorescence method, however, appears to be more robust. The oil changes its fluorescent characteristics relatively little with time, although GC analysis indicates that significant weathering has taken place (Boehm et al, 1984, Cross and Humphrey, 1986). The results presented here are consistent with these observations.

THF dissolution and subsequent column chromatography of the extract separates the hydrocarbon based material into aliphatic, PAH, N-PAH and amino-PAH chemical classes and permits the characterization of subgroups of the whole oil. The gravimetric analyses suggest that the original Arrow Bunker C contained a significant portion of compounds outside of this set of compound classes, whereas the weathered oil does not appear to contain these other components. Acidic or basic materials which would be retained on the alumina column with the solvents used in our scheme may be characterized using other separation schemes. It is likely that such components could be lost during the weathering process, especially to slow dissolution.

The use of gel permeation chromatography to characterize the molecular weight distribution has not been common for environmental samples. The results indicate that the molecular weight distribution of the separated fractions does not change significantly over time, especially when compared to distribution differences between different samples. This analytical procedure may be useful to identify the presence of a particular source oil in sediments and possibly tissues. We are proceeding to analyse extracts from clams from the Chedabucto Bay area, from both oiled and unoled areas, to test this method. It is clear that the residual stranded oils are predominantly very high molecular weight material, unlikely to be utilized by organisms.

The GC data adds little to the characterization of residual oils, as the lower molecular weight materials for which the method is sensitive, are no longer present. It is clear that calculations based on GC indicators, such as the phytane content, are not valid after significant weathering has occurred (Boehm et al 1984).

The synchronous scan fluorescence data indicates that this method remains useful after significant weathering has occurred. The spectral characteristics do not appear to change, although some of the polycyclic aromatic compounds responsible for the fluorescence are no longer identifiable by GC. This result supports the view that the compounds usually quantified by GC/MS, such as the substituted naphthalenes and pyrenes, constitute only a small part of the PAH fraction, and that their absence does not imply absence of oil components. Synchronous scan fluorescence may be the best analytical method for identifying the presence of weathered oil, especially if the source oil is known and characterized. As the oil becomes more weathered, however, the practise of referring to the measured concentrations in terms of "source oil equivalents" becomes less realistic.

Other stranded oils are presently being examined, as are extracts from animals collected in the vicinity of stranded oils. No estimate of the bioavailability of the stranded oils has yet been possible.

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OIL ENTRAINMENT BY BREAKING WAVES

by

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INTRODUCTION

Laboratory experiments were conducted employing a wind-wave facility to study the dispersion of an oil film on the water surface. The purpose of this study was to better understand the dispersion process and to investigate, to the extent possible, the validity of assumptions made in oil slick dispersion models. The laboratory environment was selected because of its convenience and also because it facilitates the measurement of physical quantities that are difficult if not impossible to measure in the ocean environment. In order to draw useful conclusions from these experiments, it is necessary to understand the physical processes in both the laboratory and ocean environment. In view of the fact that little is known about oil dispersion, several of the conclusions are somewhat speculative.

The laboratory conditions in the wind-wave facility were established by releasing oil uniformly on the water surface at the upwind end of the tunnel. Wind-induced drift currents transported the oil to the test section where waves were forced to break. A variety of experiments were conducted including measurement of wind and wave parameters, oil properties, oil film thickness and oil droplet size distributions in the water.

Both experimental and theoretical investigations of the mixing process are presented. In this article they have been reported in more detail by Bouwmeester and Wallace (1986). Other pertinent information was published in last year's AMOP proceedings (Bouwmeester and Wallace; 1985). For convenience those two references are abbreviated in this article as BW85 and BW86, respectively. This paper includes a summary of the experimental data describing the wind, wave and oil conditions in the wind-wave facility, a discussion of the dispersion characteristics resulting from the wind-wave interaction, and quantitative information on oil droplet size distributions as a function of depth.

LABORATORY EXPERIMENTS

The wind-wave facility employed for these experiments is the Environmental Wind Tunnel at Michigan State University. The wind tunnel (Fig. 1) is of the closed-circuit type; it is 17 m long and has a 1-m square cross-section not including the plexiglass water channel which is 0.3 m deep. Waves were generated at the upwind end of the test section by a variable frequency/amplitude wave maker and by wind. The mean water level in the channel was kept at 0.215 m.

The wind-wave conditions were such that waves would start to break at a fetch of 7.0 m, just before the section in which the water channel width gradually was reduced from 1 m at a fetch of 7 m to 0.72 m at 16 m (Fig. 2). This was accomplished by a 30 cm vertical wall which was installed on one side of the channel only. Breaking waves in this contraction would continue

to break intermittantly because of the energy transfer from the wind to the waves and the decreasing channel width.

Oil (diesel oil no.2) was released steadily and uniformly across the width of the channel on the water surface at the upwind end of the channel. The oil travelled downwind and entrained partially because of wave breaking in the contraction. Water was added at the upwind end and oil and water were drained at the downwind end through slots in the ramp which acted as a wave energy dissipator; the resulting mean velocity in the channel was 0.003 m/s. The oil-water mixture was separated and the oil was returned to the oil supply.

Three wind-wave-oil conditions were tested. The wind and wave conditions were kept essentially the same and the oil release rates were varied from 0.0, 0.053 and 0.145 liter per second. Differences in wind and wave conditions were only a result of the presence of oil on the water surface.

WIND, WAVE AND OIL CONDITIONS

Extensive wind, wave and oil data were collected at fetches between 7 m and 16 m. The experimental and analytical procedures are described in BW85 and BW86. The pertinent results of the experiments have been summarized in Table 1.

The oil had been repeatedly used in the facility prior to the experiments that yielded the results listed in Table 1. As a result, the oil used for the final experiments was quite stable. It is noted that the initial viscosity was 2.32×10^{-4} m/s and the initial specific gravity 0.840. The interfacial tension and surface tension of the oil conditions did not change significantly over time.

The waves with a length of 0.39 m were essentially deepwater waves. The wave measurements were used to generate wave spectra and probability density functions of the surface elevation at different fetches (See BW85). Figure 3 shows a series of these probability distributions for different oil conditions. The near sinusoidal shape of the wave resulting from the wave-maker is very apparent in the two peaks at the extreme ends in several of the distributions shown. This is particularly so at a fetch of 7 m. At larger fetches the larger surface elevations become more irregular as a result of the breaking. This effect is most significant in the absence of oil on the water surface. The data suggest that the wave breaking started at larger fetches when oil was present on the surface.

The wind conditions were based on eight velocity profiles. The shear velocity was estimated by fitting the logarithmic velocity distribution to the lowest portion of the velocity profile. The lowest velocity measurements were taken at 4 cm above the mean water level. It is possible that a slight overprediction of the shear velocity resulted. The value of the roughness in relation to the shear stress indicates that the surface is rough and that flow separation at a wave peak occurs.

Table 1. Wind, Wave, and Oil Conditions

Physical Quantity	Measured Value	Standard Deviation	Number of Measurements
<u>Oil Conditions</u>			
Oil density	SG = 0.857	0.17%	12
Oil viscosity	$\nu = 2.64 \times 10^{-5} \text{ m}^2/\text{s}$	1.2%	12
Oil surface tension	$\sigma = 29.3 \text{ mN/m}$	0.6%	12
Oil-water interfacial tension	$i = 50.5 \text{ mN/m}$	2.5%	12
Oil film thickness:			
condition II	$t = 0.15 \text{ mm}$	60%	92
condition III	$t = 0.55 \text{ mm}$	60%	92
Oil concentration:			
condition II	$c = 55 \text{ ppm}$	49%	36
condition III	$c = 54 \text{ ppm}$	52%	32
<u>Wave Parameters</u>			
Rms of wave height:			
fetch $x = 7.0 \text{ m}$	$H_{\text{rms}} = 1.48 \text{ cm}$	6.6%	7
$x = 9.0 \text{ m}$	$H_{\text{rms}} = 1.39 \text{ cm}$	18%	7
$x = 11.0 \text{ m}$	$H_{\text{rms}} = 1.44 \text{ cm}$	7.6%	6
$x = 13.0 \text{ m}$	$H_{\text{rms}} = 1.37 \text{ cm}$	3.2%	6
Carrier wave period:	$T = 0.5 \text{ s}$		
wave length:	$L = 0.39 \text{ m}$		
<u>Wind parameters</u>			
shear velocity	$U_* = 0.49 \text{ m/s}$	14%	8
Velocity at $z = 10 \text{ cm}$	$U_{10} = 6.57 \text{ m/s}$	2.0%	
surface roughness	$Z_o = 0.52 \text{ mm}$	68%	

TURBULENT MIXING IN THE PRESENCE OF BREAKING WAVES AND WIND

Breaking waves cause oil to be entrained into the water. The turbulence and the wind-induced drift current disperse the oil droplets horizontally and vertically. On the other hand, buoyancy forces drive the oil droplets back to the surface. The size distribution of oil droplets can be described as a function of depth. The prediction of these distributions requires information on the turbulence characteristics.

The mixing property of the turbulence may be characterized by the eddy diffusivity K which, in turn, may be expressed, using Prandtl's mixing length hypothesis, as the product of a characteristic mixing length ℓ and a characteristic random velocity fluctuation u , i.e.,

$$K = u \ell \quad (1)$$

The characteristic length most responsible for the turbulent mixing is the length of the largest eddies or the integral turbulence length scale. The characteristic velocity is the velocity fluctuation of those large scale eddies. Since direct turbulence measurements beneath waves are extremely difficult, heuristic arguments are used to obtain crude estimates for u and ℓ . In light of the experiment carried out by Wu (1968), the wind-induced drift current is first treated as a turbulent boundary layer extending over the full depth. Further, it will be assumed that the largest eddies vary in size according to

$$\ell = kz(d-z)/d \quad (2)$$

where d is the channel depth and $k = 0.4$. The average length scale across the depth is then,

$$\ell = 0.067d \quad (3)$$

The large eddy velocity fluctuation is assumed to be the shear velocity U_* in the water. Assuming shear stress continuity across the air-water interface,

$$u = U_{*water} = \sqrt{\rho_{air}/\rho_{water}} U_{*air} \quad (4)$$

Using the data given in Table 1

$$u = 0.017 \text{ m/s}$$

In order to include the turbulence generated by wave breaking, an energy balance including the turbulent kinetic energy (TKE) is considered. It is assumed that the length scale is not altered considerably, but that the velocity scale increases due to wave breaking. The approach will be to estimate the velocity scale by equating the energy dissipation to the TKE production by energy transfer from the wind to the water and wave breaking.

The work rate done by the wind per unit area may be estimated by

$$\dot{W} = \tau V, \quad (5)$$

where τ denotes the wind stress and V a velocity scale which, in case of a rough surface, is equal to the phase speed of the roughness elements

(Stewart and Grant 1962). The dominant roughness elements in our case are the steep carrier waves. Hence, with $\tau = \rho_{\text{air}} U_*^2$,

$$\dot{W} = \rho_{\text{air}} U_*^2 C \quad (6)$$

where C is the phase speed: $C = gT/2\pi$. Hence,

$$\dot{W} = \rho_{\text{air}} g T U_*^2 / 2\pi \quad (7)$$

A portion of the energy provided by the wind goes to the wave energy. But because the waves are in a condition of incipient breaking, it is assumed that an equal amount of the wave energy is lost through breaking. Further, it is assumed, following Longuet-Higgins (1969), that the main portion of the energy released by breaking goes directly into turbulence.

Because the waves are at a point of incipient breaking, the wave energy per unit area does not vary significantly along the length of the tunnel. This is supported by the wave data presented in Table 1. Therefore, the wave energy transport by the waves is proportional to the cross-sectional area of the contraction. The decrease in wave energy transport per unit length and per unit width is given by

$$\Delta F = C \rho_{\text{water}} g^2 H_{\text{rms}}^2 db/dx(1/b), \quad (8)$$

where C is the group velocity, b is the channel width and db/dx is the rate at which the channel width decreases with distance. The group velocity of deep water waves $C = gT/4\pi$, therefore,

$$\Delta F = \rho_{\text{water}} g^2 T H_{\text{rms}}^2 db/dx/(1/4\pi b) \quad (9)$$

Since we assume that the wave energy is constant within the contraction the lost wave energy goes to TKE.

The TKE dissipation rate per unit mass D is related to the length and velocity scales of the large scale eddies and may be estimated (Tennekes and Lumley, 1972) as

$$D = u^3 / \ell \quad (10)$$

Thus, the dissipation rate per unit surface area, after substitution of Eq. 3, becomes

$$D_A = 15 \rho_{\text{water}} U^3 \quad (11)$$

Equating the TKE production ($\dot{W} + \Delta F$) to TKE dissipation (D_A) leads to the following equation for u :

$$u = \left[\frac{1}{60\pi} g^2 T H_{\text{rms}}^2 \frac{1}{b} \frac{db}{dx} + \frac{1}{30\pi} \frac{\rho_{\text{air}}}{\rho_{\text{water}}} g T U_*^2 \right]^{1/3} \quad (12)$$

Using the previously given data, the characteristic velocity is

$$u = (0.0000016 + 0.0000150)^{1/3} = 0.0255 \text{ m/s}$$

This value is, as expected, higher than the value calculated using Eq. 4 which does not include the wave breaking conditions.

The eddy diffusivity in the contraction is now estimated using Eq. 1, 3 and 12, to be

$$K = 0.00037 \text{ m/s}^2. \quad (13)$$

It was reported in BW85 that the longitudinal dispersion coefficient was 0.012 m/s. This is a factor 32 times as large. This is less than the theoretical results predicted by Elder (1954) whose work indicates that the ratio between the eddy diffusivity and longitudinal dispersion coefficient is about 90 for turbulent flow down an inclined plate. The turbulence enhancement due to wave breaking appears to explain, at least partially, the discrepancy.

Thus far, it was assumed tacitly that the integral time scale of the larger eddies was large enough that the turbulence characteristics would not change in time. To verify this assumption the average time interval between breaking events was compared with the integral time scale. The integral time scale is

$$T_t = l/u \quad (14)$$

which is 0.56 s. The measured average breaking interval was about 8 s for both conditions II and III. Hence, the data suggest that the turbulence has a certain degree of intermittancy. More research is needed to evaluate the significance of this observation.

OIL DROPLET SIZE FORMATION AND DISTRIBUTIONS

The oil released at the upwind end of the tunnel travels downwind as a film on the water surface. At a fetch of about 5 m some of the waves start to break so that oil is entrained into the water. But it is not until the oil reaches a fetch of 8 m that the wave breaking reaches its maximum intensity. The surface oil at this fetch is no longer uniformly distributed but is present as patches and streaks consisting of many oil globules. Breaking waves continue to redistribute the surface oil and entrain a portion into the water. Because of buoyancy forces large droplets tend to be concentrated in the upper layers beneath the waves; the smaller droplets penetrate to larger depths.

Droplet size distributions were measured at a depth of 0.16 m for two oil release rates (conditions II and III; see Table 1) using a technique described by Wallace et.al. (1986). These data are presented in Fig. 4a and b. The smallest measured droplet size was 12×10^{-6} m and the largest droplet size was 0.50×10^{-3} m. There is clearly an exponential decrease in number of droplets with diameter. Visual observations indicated that larger droplets occasionally appeared at larger depth. However, they do not contribute significantly at this depth to the total oil concentration.

A simple droplet distribution model to predict droplet size distributions and total concentrations as a function of depth may be based on the assumption that equilibrium conditions exist under which the rise of oil due to buoyancy equals the downward transport due to turbulent mixing, i.e.,

$$K \frac{dC_i}{dz} = -R_i C_i \quad (15)$$

where C_i is the concentration (volume of oil per volume of water) of droplets with diameters between $d_i - \Delta d/2$ and $d_i + \Delta d/2$ and R_i is the rise velocity of droplets in this interval. C_i is given by

$$C_i(z) = \pi d_i^3 N_i(z)/6 \quad (16)$$

where N_i is the number of droplets per unit volume in the interval R_i depends on the droplet Reynolds number Re . Following Raj (1977)

$$R_i = \begin{cases} \frac{g}{18\nu_w} d_i^2 (1-\Delta) & Re < 50 \\ \left[\frac{8g}{3} d_i (1-\Delta) \right]^{1/2} & Re > 50 \end{cases} \quad (17)$$

where Δ is the oil to water density ratio.

Given the number of droplets N_i^* or the corresponding C_i^* at a depth z^* the solution of Eq. 15 is found to be

$$C_i(z) = C_i^* \exp(-R_i(z-z^*)/K) \quad (18)$$

The measured droplet size distributions and the simple droplet size distribution model can now be used to predict the droplet size distributions at various depths. We assumed several relationships between the droplet diameter and number of droplets just below the water surface. Those relationships were then used to predict the droplet size distribution at the depth where the data Fig. 4a and b were obtained. Relatively good approximations were found with the following relationship:

$$[N_i d_i]_{z=0} = \text{constant} \quad (19)$$

Figure 5a and b show the results of this analysis.

Eq. 19 provides insight into the droplet formation process. It appears that the number of oil droplets formed is inversely proportional to the droplet diameter.

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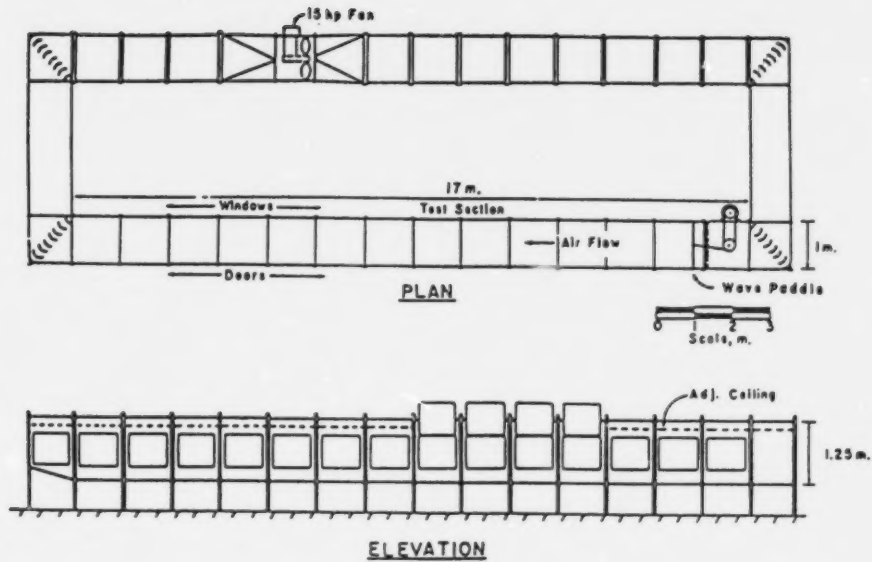


Figure 1. Environmental Wind Tunnel (EWT) at Michigan State University

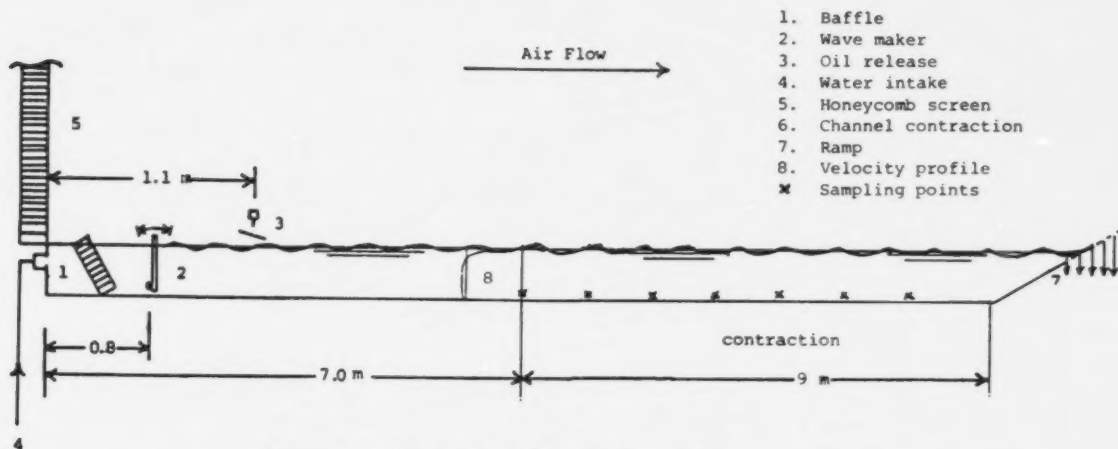


Figure 2. Schematic of Test Section of EWT

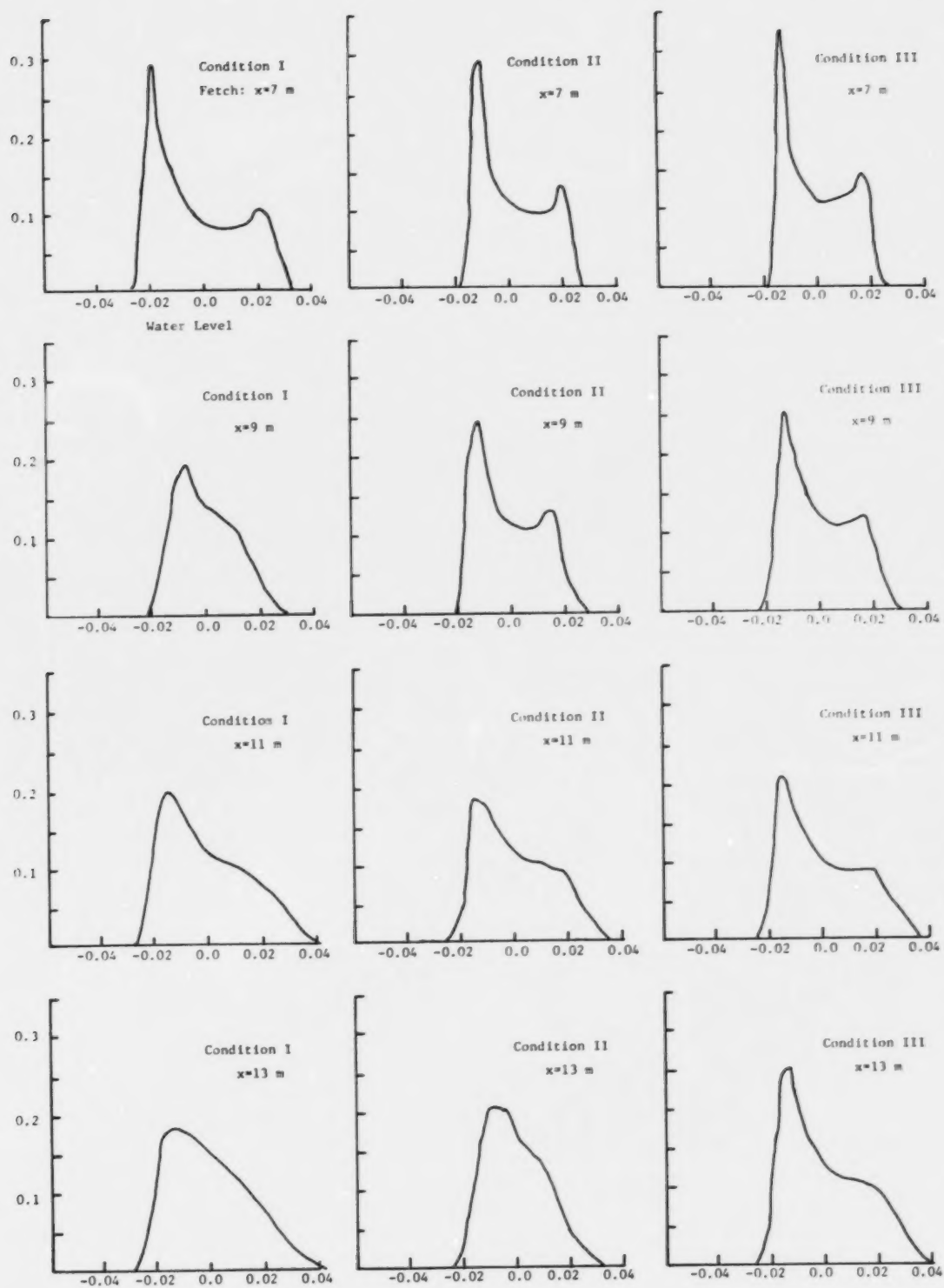


Figure 3. Probability Density Functions of Water Surface Elevation.

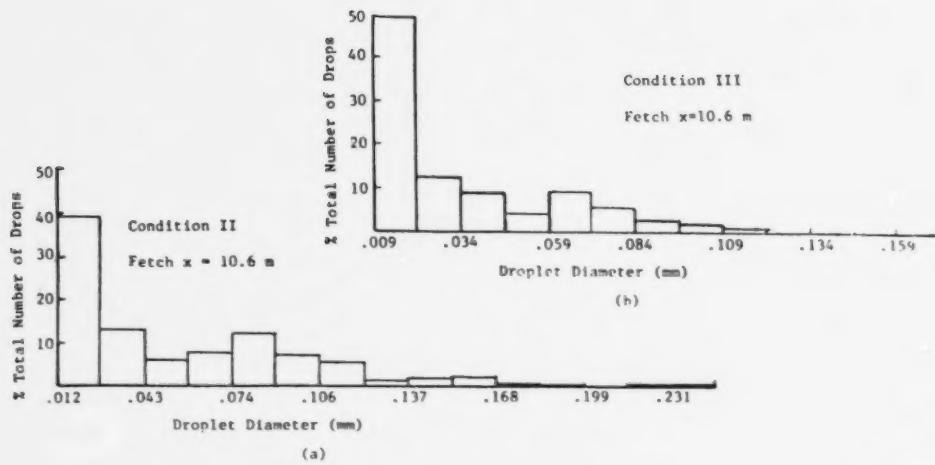


Figure 4. Measured Droplet Size Distributions

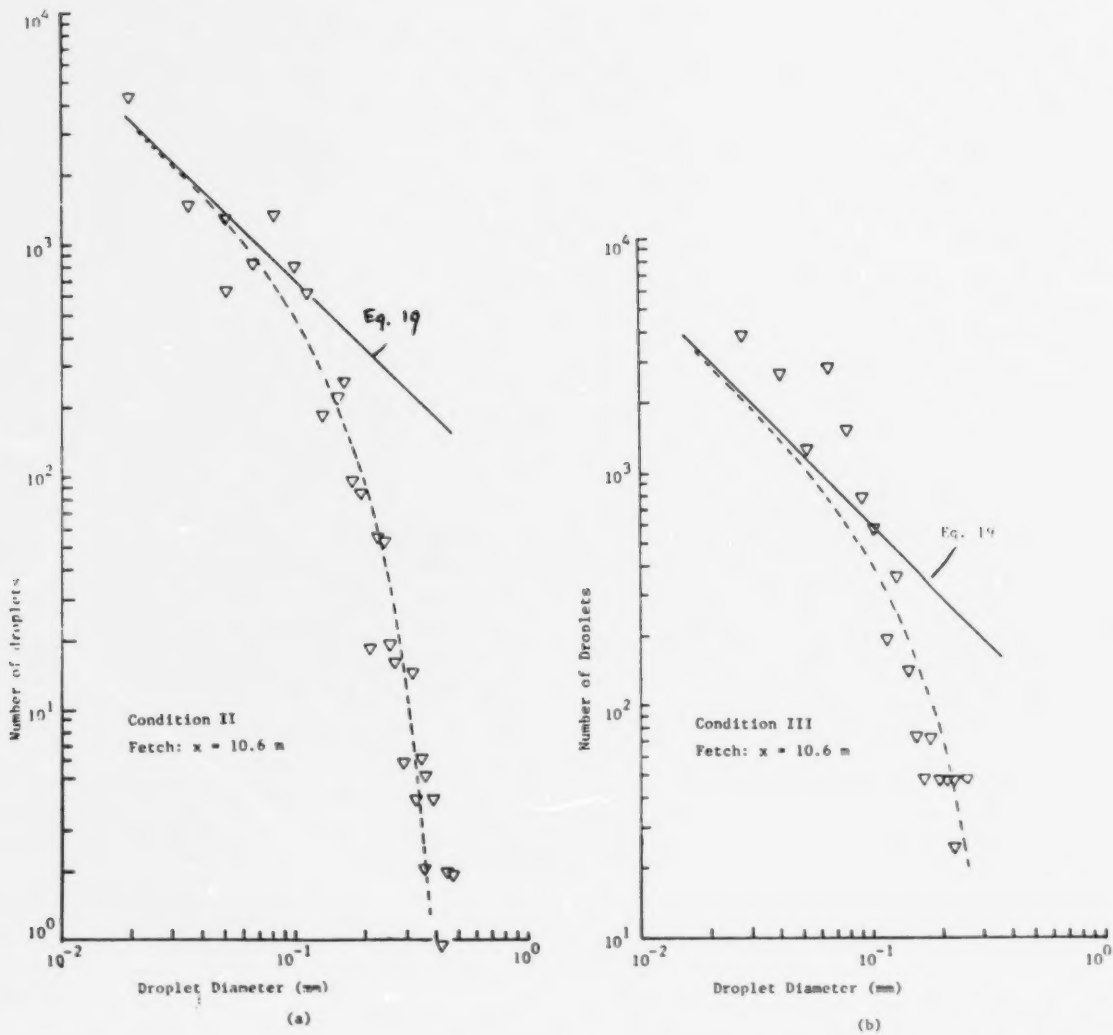


Figure 5. Calculated (-----) and Measured (▽) Droplet Size Distributions

THE BEHAVIOUR OF OIL IN FREEZING SITUATIONS

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ABSTRACT

An experimental study of the behaviour of an oil spill in a developing (grease) ice field is described. It was found that significant quantities of oil may be entrained within and beneath a grease ice field. The amount of oil entrained is increased by

- i) a high oil density occurring naturally or induced by weathering.
- ii) the presence of sufficient turbulence to disperse the surface oil at an appreciable rate and induce mixing within the forming ice field.
- iii) a high oil viscosity occurring naturally or induced by weathering.
- iv) the formation of emulsions of sea water and/or ice in the oil.
- v) the formation of smaller oil droplets.
- vi) the formation or coalescence of ice particles to a size of approximately 5 mm in diameter.

It is suggested that the results and observations obtained here be used as a component in an "expert system" computer model that would aid in the prediction of the fate and behaviour of an oil spill in the presence of a developing ice field and in other regimes in which oil may interact with ice. This model may then be included as part of a comprehensive model encompassing the entire spectrum of oil spills conditions which may occur in the Arctic marine environment.

INTRODUCTION

The exploration and development of the Arctic as an important petroleum producing region has resulted in a significant number of research programs pertaining to the presence of oil in the Arctic environment. In particular, much effort has been devoted to modeling, environmental assessment, countermeasures and recovery of oil spills in Arctic waters. However, while detailed studies have been performed and models proposed with regard to oil spills underneath ice, above ice and in open waters, very little research has been performed on the topic of spills in freezing conditions, or on the interaction of oil with a developing ice field. The purpose of this study is thus to investigate and quantify the nature of the oil and developing ice field interactions. The knowledge gained with regard to this phenomenon may be used to assess possible countermeasures or clean up techniques for the oil. It is also intended that the data accumulated may be used to formulate a predictive model for the behaviour and fate of oil spilled in a developing ice field.

Existing oil spill models, as reviewed in previous AMOP Technical Seminars, (Mackay, 1984) tend to fall into certain defined classes such as (i) open-water trajectory models which may include interaction with shorelines, (ii) open-water behaviour models which describe the changing properties and

configuration of oil spills with time, (iii) descriptions of oil behaviour on shore, (iv) descriptions of behaviour in rising plumes reaching the sea surface or ice under surface, (v) descriptions of oil movement under ice and entrapment in ice and subsequent release during thaw. As has been pointed out by Bobra and Fingas (1986) there is a lack of model capability treating the situation in which a spill on water is subjected to freezing conditions. Behaviour in leads has also been studied (MacNeil and Goodman, 1985), but there remains a need to quantify the processes of oil splashing onto or under ice and determine the extent of emulsification and weathering.

It is believed that there is also a need to develop an overall modelling capability which can bring together these various models in one system and allow the user to predict oil spill behaviour under a wide variety of situations - open water, shorelines, and ice of various conditions and thus exploit the considerable experience which has been built up over the years in programs such as AMOP. In effect, this would be close to an "expert system" which has been successfully used in fields such as medical diagnosis and shows promise of applicability to environmental emergencies as discussed recently by Hushon (1986).

This study thus has several facets. At the most general level it will attempt to provide a structure for an expert oil spill modelling system and assess the feasibility of that system. This aspect is not reported here. There are more specific components being considered such as oil behaviour in open water (based on past work), oil behaviour at shorelines (based largely on the work of others such as Gundlach *et al.* in these and previous proceedings, e.g. Gundlach *et al.*, 1985) and oil behaviour in the presence of ice (based on the work of many authors). As one of these components we have studied and report here experimental work on oil behaviour in developing ice fields, which we regard as contributing one component of the overall system.

OIL INCORPORATION IN DEVELOPING ICE

The pertinent question in this study is that of whether, and how, oil may become incorporated within the developing or "grease" ice, hence removing it from sight and from access to most conventional recovery processes. The theory underlying the phenomenon of oil incorporation in a developing ice field is multi-faceted. An ice field's ability to retain quantities of oil within its structure below the surface of the water is presumably a function of the oil's density, viscosity and interfacial tensions as well as the thickness of the oil layer, the porosity of the ice field and the level of turbulence present. While the subsurface behaviour of oil in water has been explored to some extent by Wilson *et al.*, (1985) the presence of ice particles in water complicates the theory underlying this process. In the aforementioned paper it was demonstrated that significant quantities of oil may be entrained below the surface of the water if the upward buoyancy force exerted upon the oil particles is balanced by the downwards driving force of subsurface currents created by turbulence in the form of breaking waves or local downswelling regions. The upward buoyancy force may be quantified on the basis of a Stokes' Law analysis of the oil particles while the downwards force may be related to wind speeds directly above the water surface. Hence, a developing ice field or grease ice may be treated similarly with an ice/water mixture replacing water alone in the theoretical analysis. However, it is also necessary to consider the movement of the oil between the individual ice particles. This requires correlation of ice porosity and oil/ice/water interfacial tension with the wind

derived turbulent behaviour of the ice-water mixture. It is also necessary to correlate this information with oil properties and the dynamic behaviour of both the oil and ice with changing environmental conditions.

It appears that the number of variables affecting the process of oil incorporation in a developing ice field is sufficiently large to render a theoretical approach to this phenomenon extremely complex and probably inaccurate and inconclusive. Thus, the initial intent of this paper is to obtain a quantity of data on the probable fate of an oil spill under freezing conditions. This empirical approach will allow the prediction of probable oil-ice behaviour under various environmental conditions. In future, theoretical approaches may then be attempted to enhance the interpretation and correlation of experimental results.

EXPERIMENTAL

The principal experimental apparatus, illustrated in Figure 1 consisted of a clear lucite tank of dimensions 35 cm by 35 by 35 cm deep into which various mixtures of ice, oil and water were placed. Agitation of the mixture was obtained by use of an oscillating hoop apparatus, powered by a 12 volt battery and a D.C. motor. The hoop could be oscillated vertically at a maximum rate of approximately 120 oscillations per minute. The vertical oscillations of the hoop, just below the surface of the water-oil interface created a low energy ripple/wave effect. The apparatus was placed within a cold room in which selected subzero temperatures could be maintained.

A series of experiments was performed to investigate the phenomenon of oil incorporation in grease ice fields. Since oil density is obviously an important parameter it was desired to test a series of oils of varying density, but of relatively constant viscosity. Unfortunately weathering a crude oil results in a marked increase in viscosity. After some investigations it was decided to use a mixture of a light hydrocarbon oil and a dense organo-chlorine solvent. Bayol 35, a white oil, (SG of 0.790) was mixed with measured quantities of tetrachloroethylene (SG of 1.615) in order to vary the net oil density and was introduced into various grease ice fields. Oils of various densities and oil layer thicknesses were used as well as grease ice fields of varying ice particle diameter and field depths. The grease ice fields were not artificially compressed and were allowed to attain their own thickness and ice-to-water ratio. The experiments were carried out in large glass, graduated beakers of 2500 to 3500 mL volume and the oil was dyed red using Sudan Red dye in order to facilitate the observation of the oil incorporated within ice. The oil-ice mixture was allowed to freeze solid after which volumes of oil incorporated within the ice could be measured. Ice-to-water volume ratios within the grease ice fields were also measured by displacement of water upon introduction of ice to the water. Fresh water was used since this greatly simplifies the experimental procedure and some fresh over salt water stratification is quite prevalent under Arctic conditions especially in close proximity to rivers, icebergs or floes.

A number of experimental runs were performed in conjunction with the incorporation of oil in grease ice experiments. After oils of various densities had been incorporated into grease ice fields and allowed to freeze solid the beakers of ice and oil were placed in an ambient environment (temperature of 21° C) and allowed to thaw. Measurements of the volume of oil released as a function of time, density of oil, and extent of incorporation were obtained in order to determine the effect of the entrained oil on the

thawing process. Non-oiled ice samples were also allowed to thaw in the same ambient environment in order to compare rates of thaw of oiled and non-oiled ice.

A number of emulsions were formed under freezing conditions using a rotating shaker placed in an incubator and maintained at a temperature of -5°C . Emulsions were created using a 70/30 combination of No. 2 and No. 6 fuel oils as well as Arabian heavy crude oil. The oils were mixed with salt water in a ratio of 90% water to 10% oil. Also, a number of samples included ice crystals of various sizes in order to investigate the possibility of emulsification of oil within a grease ice field. The rotating shaker was operated at a speed of 48 rpm over a period of 3-4 hours in order to produce the emulsions. Once formed the emulsions were introduced into grease ice fields and observed. Density and percent water content were also measured.

Experiments were performed in the hoop and tank apparatus using a 70/30 mixture of No. 2 and No. 6 fuel oils with different thicknesses of oil layers in order to explore the effects of thermal insulation by the oil versus the oil's damping effect on turbulence. The hoop was operated at maximum oscillatory speed while the cold room was maintained at a temperature of -5°C . Observations were recorded and the time for initial ice formation was noted and compared with the time for ice formation in the absence of oil.

An actual spill of No. 6 fuel oil in the St. Lawrence River, Quebec, in a developing ice field, was observed in December of 1985. Oil and ice mixture samples were obtained and observed. The oil was also analyzed for density increase as a result of weathering using a densitometer at the Environment Canada River Road Laboratory in Ottawa, Ontario.

RESULTS

Figure 2 illustrates the results from the oil incorporation in grease ice experiment. The percent by volume of an oil layer, of known thickness, which was incorporated into the grease ice layer is plotted. Grease ice fields were obtained using ice particles of different size in order to simulate the coalescence and compaction of ice particles that naturally occur as grease ice becomes pancake ice. Hence, percent of the oil present which is incorporated into the ice is plotted against ice particle size with initial oil layer thickness and oil density as parameters.

The very dense oil tested, with a specific gravity of 0.98 was incorporated into the agitated grease ice field to a maximum level of 78 percent. The oil with a specific gravity of 0.92, similar to that of ice itself, was incorporated to a maximum level of 52% while the least dense oil, with a specific gravity 0.790, was incorporated to a maximum of only 47 percent. The extent of incorporation appears to reach a maximum when the ice particle size is in the range of 5 mm to 8 mm. When the ice particles are very large the extent of incorporation is considerably reduced. This appears to be a result of the effect that with larger ice particles there were larger spaces between the individual particles and hence the oil was able to flow more easily to the surface of the grease field through these gaps. Less incorporation also occurred for very small ice particles (less than 3 mm diameter). This appeared to be a result of the small particles being of insufficient diameter to "trap" oil droplets below them with the result that the oil droplets pushed through and past the ice particles as they surfaced.

For the two lower density oils tested there appears to be little variation in oil incorporation as oil layer thickness increases. However for the very

dense oil (specific gravity of 0.98) the amount of oil incorporated was reduced significantly with increasing oil layer thickness. This result appears to be related to the effect that as thicker layers of oil were introduced, the oil droplets (which dispersed throughout the grease ice as a result of agitation) tended to be much larger than those created with a thin oil layer. The thick layer drops tended to be on the order of 4 mm to 6 mm diameter while the thin layer drops were on the order of 1 mm to 3 mm diameter. Because the thick layer oil droplets were much larger their positive buoyancy driving force was greater than that for small droplets.

It appears that a simple "rule of thumb" is that the oil droplet size will be similar to the thickness of the oil slick from which they were derived.

The results from the thawing experiments are illustrated in Figure 3 as a plot of percent oil remaining incorporated within the ice as a function of the time that the oil-ice mixture has been exposed to an ambient environment. Oil density is the parameter.

The deviation from linearity of the plots after as short a time as 5 hours is probably a result of the growing oil layer on top of the ice. Because the oil was less dense than the ice it remained on top of the ice once released from within the ice. The oil then insulated the ice from the warm environment and retarded the rate at which the ice thaws and hence slows down the rate at which oil is released from the ice.

The curves plotted show that the denser oils required significantly larger amounts of time to be released from the ice.

Exploratory experiments were performed to observe the effects of oil incorporation on the actual rate that the ice thaws. However, in no case was the oil layer completely incorporated within the ice and hence the situation reverted to the case of ice with an oil film above it which has previously been studied by other authors.

An emulsion of Arabian heavy crude and salt water was formed which had a net specific gravity of 0.946 and was composed of approximately 40% salt water and 60% oil. The emulsion was obtained after three hours of shaking at 48 rpm. It is possible that more vigorous shaking would have produced a higher water content and hence higher specific gravity emulsion. The emulsion was not highly stable and remained in emulsified form, in the absence of ice, for only about 50 hours.

The emulsion was poured into a grease ice field within a 3500 mL beaker and stirred. Figure 4 is a photograph of the resulting emulsion in ice incorporation. It was observed that the oil bubbles incorporated within the ice field were much larger than those formed using low viscosity oils. The high viscosity oil droplets were as large as 10-20 mm in diameter. Continuous agitation reduced many of the oil droplets to a size as small as 5 mm in diameter. However, the relatively large size of the emulsified oil droplets prevented their movement upwards through the ice field. An estimate of the amount of oil incorporated was obtained by pouring the remaining surface layer of oil into another beaker. The amount of oil incorporated was measured as 80% to 90% of the initial quantity.

In order to investigate the effect of oil on the growth of the turbulent ice fields tests were performed using the principal experimental apparatus and a 2 mm layer of the 70/30 No. 2 and No. 6 fuel oils mixture. Turbulence was provided by the oscillating hoop mechanism. While the expected frazil/grease/pancake ice formation was not noted, a slushy, crystal-like, porous frozen mixture initially formed which trapped significant quantities of oil within its internal structure. Below this layer, columnar ice formation was

observed and in the first few cm of columnar ice round oil droplets of varying diameter became trapped within the growing ice. The droplets of oil ranged in diameter from as small as 0.5 mm to as large as 10 mm. The upper layer of the ice-oil mixture was solid but porous in nature with the pores in the ice containing significant quantities of oil. During the early period of the freezing process the oil was wave driven downwards by the hoop and would then resurface due to its positive buoyancy in the water. However, as freezing progressed, the ice chunks formed and then broken by the hoop became more numerous and hence formed a thicker mixture in the oil and water. This broken ice increasingly inhibited the ascent of the oil to the surface. However the oil of initial specific gravity 0.919 was sufficiently close to neutral buoyancy to allow the entrainment of large quantities of oil within the first 10 cm layer of water and ice by the downward motion of the hoop. Shortly thereafter the ice and water mixture was of sufficient consistency to trap even large droplets of oil and also allow the formation of columnar ice around and beneath the oil. The resulting oil-ice mixture was of porosity such that when pressure was exerted downwards upon it oil would flow upwards through pores and channels within the ice.

The wave or ripple effect produced by the hoop was not of sufficient energy to break up the oil layer except about the actual perimeter of the hoop. Because of this, it was not possible to quantify the balance between the oil's insulating, ice growth retarding, behaviour and its wave dampening, ice promoting behaviour. The experiments performed support the suggestion that the oil layers of thickness that would be expected in an actual spill would not be of sufficient depth to dampen swells of the magnitude expected in an ocean. Oceanic wave action is expected to break up the oil slick and hence severely retard its ability to dampen waves and insulate the water below from the subzero atmosphere. While the times recorded for wave formation are not believed to have a high degree of accuracy there was no significant difference between time for ice formation in the presence or absence of a thin oil layer under turbulent water conditions.

Matane Spill

As previously noted a spill of No. 6 fuel oil occurred in the Gulf of St. Lawrence River in December of 1985. The author (David G. Wilson) was able to travel to the site of the spill and arrived three days after the spill had occurred. At that time, for a width of about five metres from shore, there existed a mixture of grease and pancake ice and for the next twenty metres a mixture of frazil and grease ice. The spill occurred about 100 m offshore and was blown into the grease/pancake ice mixture by the wind and current of the river. At the time of observation no oil was visible within or above the grease ice and the only visible oil was that washed up on shore. The oil washed up on shore was grease ice that had been compressed and had the water forced from between the individual ice particles by the pressure of the ice against the shore. The result was a porous crystalline ice-oil mixture that contained up to 50% oil. Figure 5 is a photograph of the ice-oil mixture which was observed at the shoreline. Samples of the oil were analyzed at the Environment Canada River Road Laboratory in Ottawa on a Parr densitometer. Table 1 provides a summary of the results. The specific gravity of the oil near freezing temperatures is quite close to that of the sea water at the spill site which was estimated to be 1.02. This raises the possibility that although there was no oil visible from above the grease and frazil ice there may have been large quantities of oil below or within the ice. There was also a high

level of turbulence in the water during the period of the spill and hence it is possible that water-oil emulsions may have been formed.

Table 1

Temperature (°C)	D E N S I T Y	
	Sample 1	Sample 2
25	0.9996	1.0020
20	1.0033	1.0061
15	1.0073	1.0098
0	1.0178	1.0204

CONCLUSIONS

A series of experiments has been performed which investigate the phenomenon of oil entrainment within a developing ice field. The observations recorded from the laboratory experiments have been complemented by observations from an actual oil spill during freezing conditions.

It is concluded that significant quantities of oil may be entrained within a developing ice field under freezing conditions. The extent of incorporation is enhanced by:

- i) a high oil density occurring naturally or induced by weathering.
- ii) the presence of sufficient turbulence to disperse the surface oil at an appreciable rate and induce mixing within the ice field.
- iii) a high oil viscosity occurring naturally or induced by weathering.
- iv) the formation of emulsions of seawater and/or ice in oil.
- v) the formation of smaller oil droplets.
- vi) the formation or coalescence of ice particles to a size of approximately 5mm in diameter.

It is concluded that under non-turbulent water conditions an oil layer will behave as an insulating layer and retard ice development beneath it. Under turbulent water conditions it is likely that the presence of oil will have a negligible effect on the development of ice except for its possible incorporation within the developing ice.

Furthermore it appears that solar radiation has little effect on the development of an ice field in the presence of oil unless environmental conditions are non-turbulent. In such a case solar radiation may significantly retard the ice formation process.

The least buoyant oils (of highest density) will require the greatest amount of time to be released from a frozen ice pancake during the thawing process. Once the oil begins to collect on the surface of the ice, solar radiation will tend to hasten the thawing process.

It has been suggested that an empirical and theoretical approach be taken to model the process of oil incorporation within a developing ice field in order to predict the extent of oil entrainment under given circumstances.

Finally, it is believed that this study will contribute information concerning one component of the overall expert oil spill modeling system. The structure and success of that system remains to be assessed.

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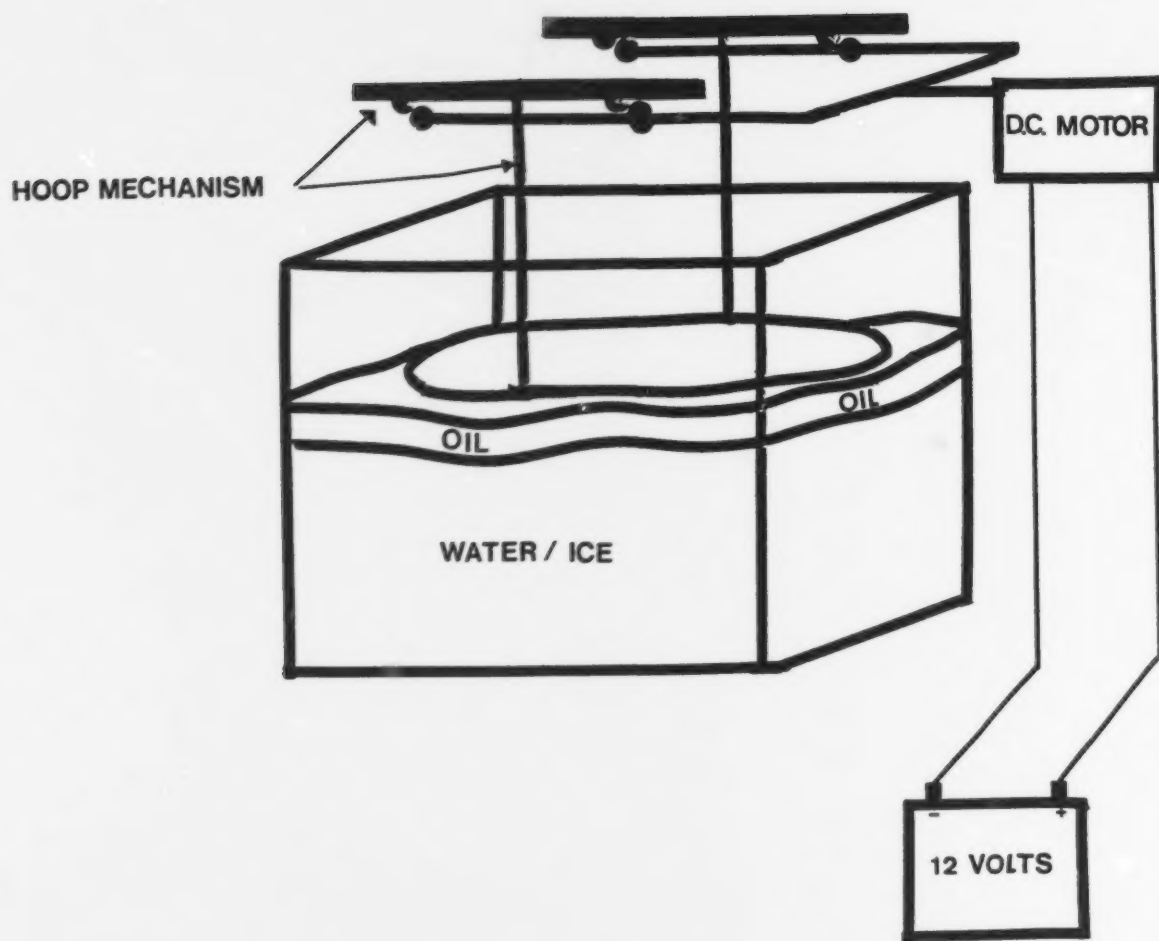


FIGURE 1

OSCILLATING HOOP AND TANK APPARATUS

OIL/ICE INCORPORATION

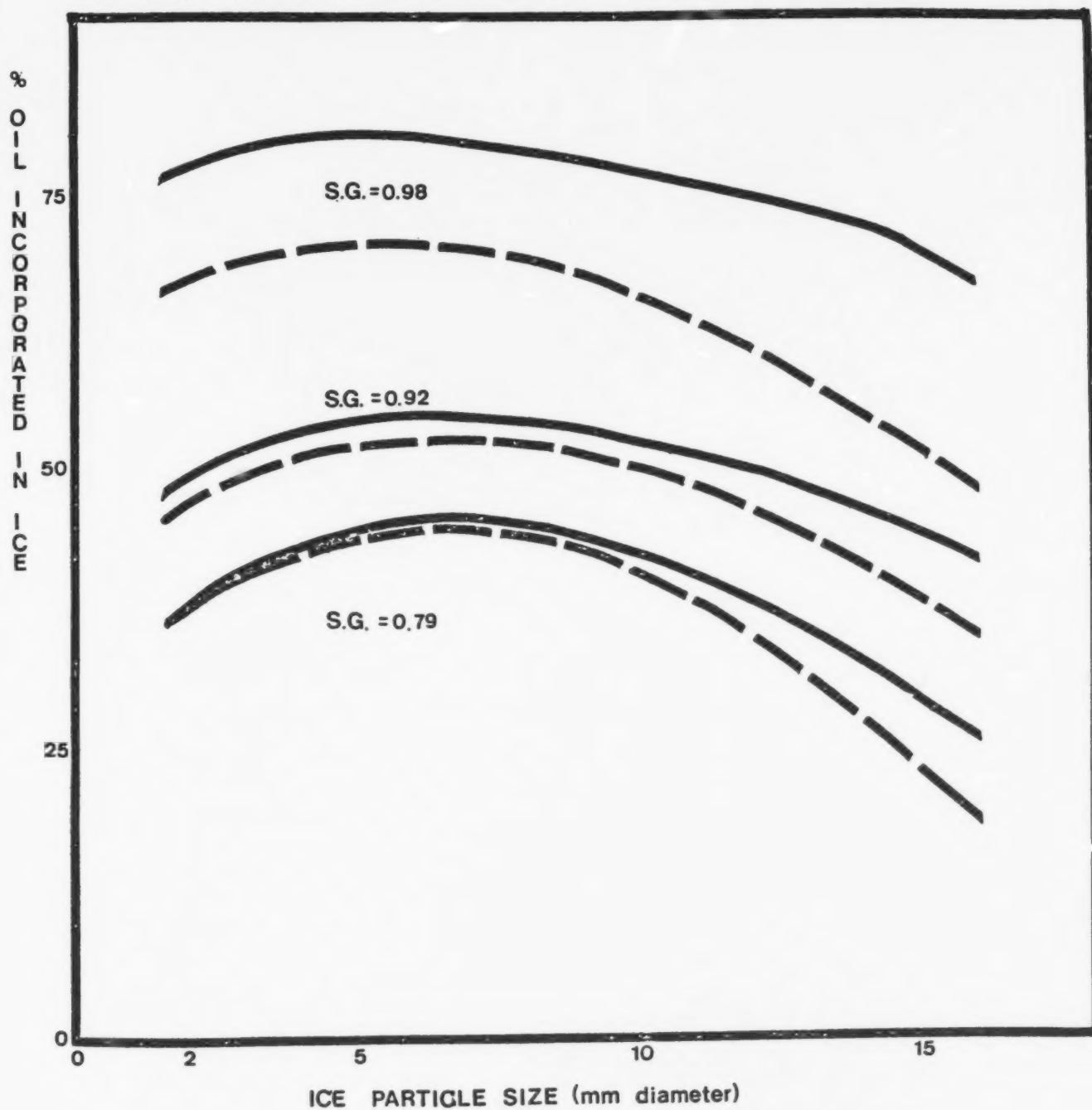


Figure 2

Plot of % Oil Incorporated vs. Ice Particle Size

LEGEND:



OIL LAYER THICKNESS

2 mm

5 mm

OIL/ICE THAW BEHAVIOUR

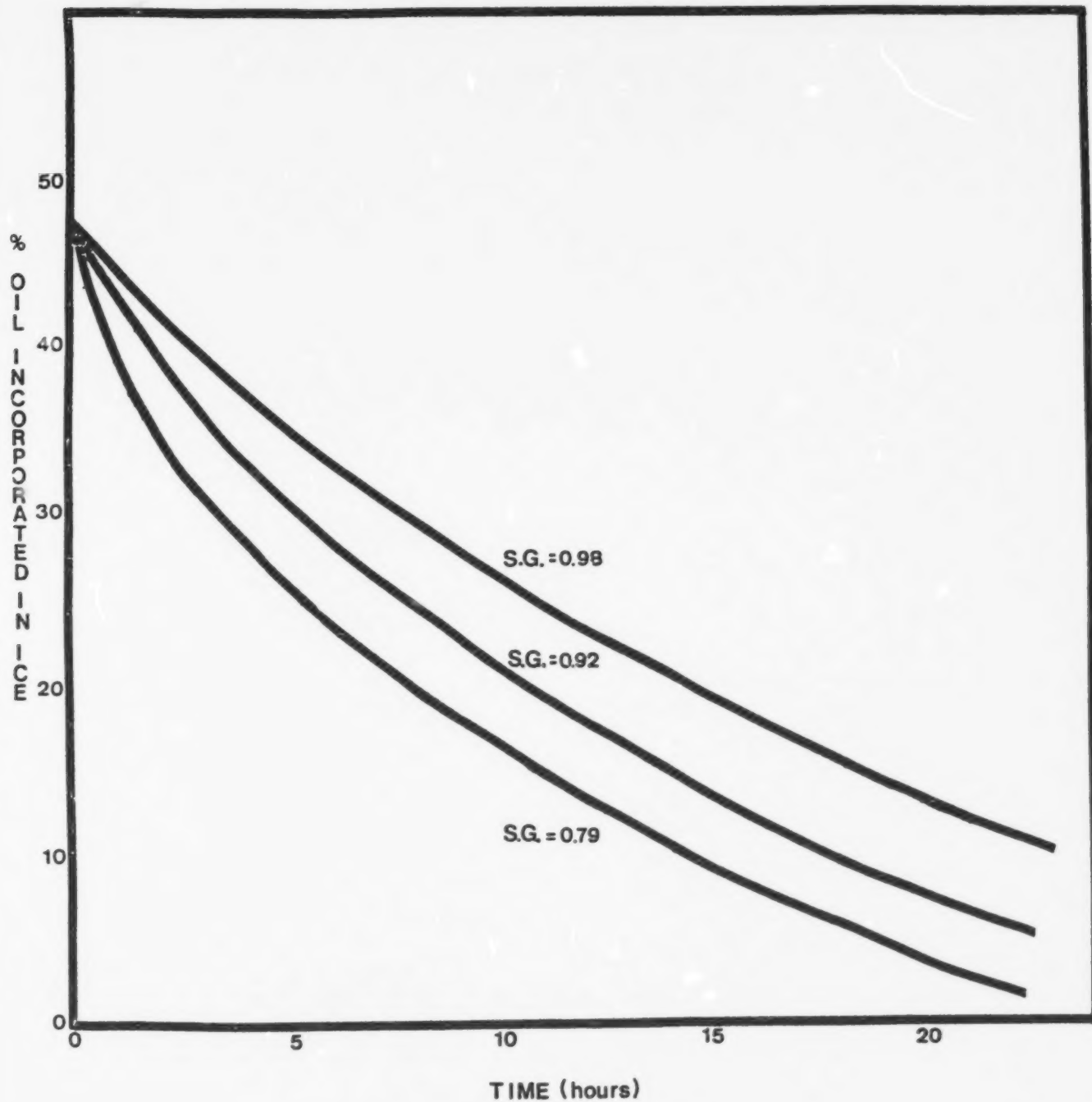


Figure 3

Plot of % Oil Incorporated in Ice vs. Time During Thawing of Oil/Ice Mixture

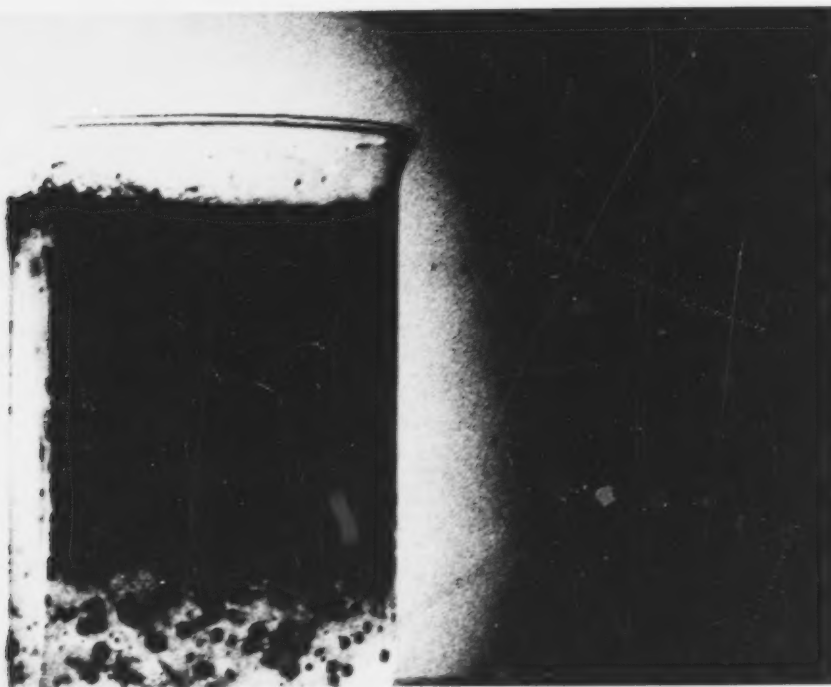


Figure 4 Water-in-oil Emulsion Incorporated in Dense Grease Ice.

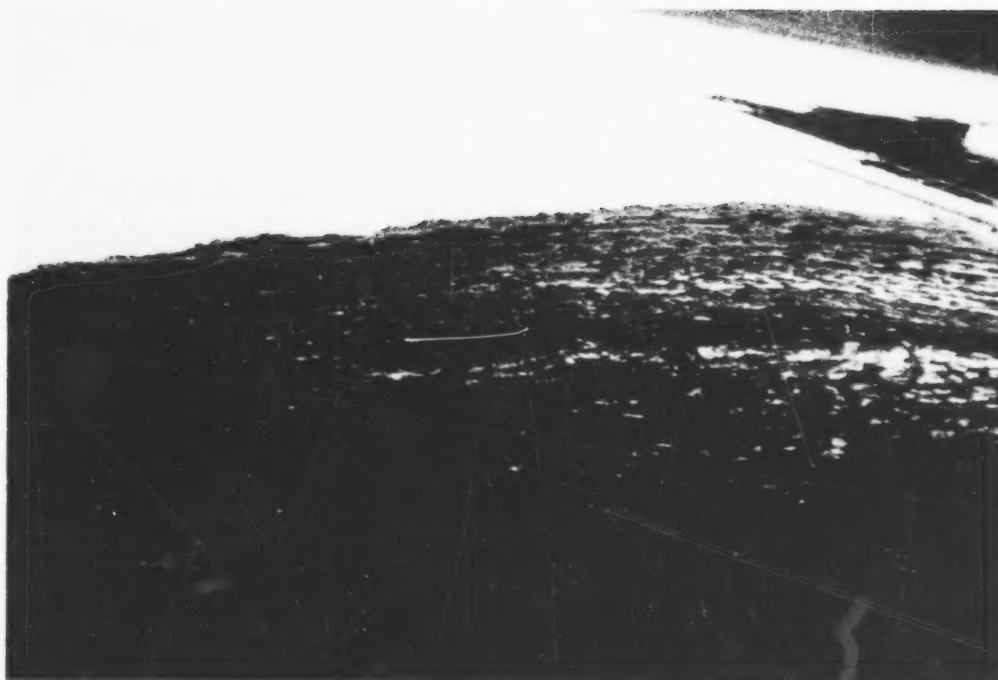


Figure 5 Oil/Ice Mixture After Matane Oil Spill

QUANTIFICATION OF OIL DEPOSITION AND REMOVAL RATES FOR A SHORELINE/OIL SPILL INTERACTION MODEL

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ABSTRACT

Under sponsorship of U.S. Minerals Management Service in Anchorage, Alaska, preliminary development of a computer-based model representing oil/shoreline interactions has been completed. Coastal environments have been divided into seven types: exposed rocky shores, sand beaches, gravel beaches, sheltered rocky shores, peat scarps, tidal flats, and marshes/wetlands. Oil impact on a specific shoreline segment is determined by other aspects of the model based on winds and currents. Once onshore, oil persistence is determined by tidal level and a removal coefficient for each shoreline type (subdivided into beach face and backshore for sand and gravel beaches). A verification program, including model testing using *Amoco Cadiz* data and the collection of surf-zone data (but no oiling) in Bristol Bay, is planned for 1986.

INTRODUCTION

Oil spill models currently bring oil adjacent to but not onshore. This paper presents a framework whereby oil deposition and removal can be modeled under varying shoreline and wave conditions. The approach is based primarily on observations of actual spill incidences as well as the BIOS (Baffin Island Oil Spill) field oiling study. Although the framework will likely remain as presented, the removal coefficients herein suggested may change as the model is tested and refined, and as more information becomes available.

The development of this model is sponsored by the U.S. Department of Interior, Minerals Management Service, OCS Study MMS 85-0098. This shoreline interaction model component will be linked with at least three other model components--offshore trajectory, chemical weathering, and surf-zone and sediment transport. Application of the complete model, called SMEAR, is planned for Bristol Bay, Alaska, and therefore, the text primarily discusses cold-water regions. As designed, the oil/shoreline model (1) is generic in application, yet specific enough to be applied to the Bristol Bay region; (2) takes into account different shoreline environments; (3) indicates spilled oil persistence and refloating; and (4) incorporates oil weathering through use of the aforementioned weathering model.

SHORELINE CLASSIFICATIONS

In order to develop an oil/shoreline interaction model, some basic information concerning the shoreline types to be affected is necessary. Few nationwide, or even regional, coastal classification systems currently exist. Fortunately, several geomorphic-based classifications are available as a result of oil-spill planning work. Over the past seven years on the U.S. side, primarily through the support of MMS and NOAA, a detailed shoreline classification scheme was developed to aid response to oil spills (Gundlach and Hayes, 1982). Currently, the areas mapped now encompass much of the coastal habitats of the United States as well as several Great Lakes areas of Canada. This system classifies shorelines into a minimum of ten types (which are then ranked in order of potential oil-spill damage). Other classification schemes [e.g., Woodward-Clyde Consultants (1981) for arctic Alaska, (1982) for northern California, and (1984) for the Chukchi Sea; and ABSORB (1983) for the Beaufort Sea], as well as the extensive classification work in Canada [e.g., McLaren (1980) and Owens (1977, 1979)], can also be converted into a model format. Although the exact shoreline types vary somewhat between, for example, the northern Bering Sea and south Florida, the majority of types remain the same from region to region.

For the oil/shoreline model, seven major shoreline types would be utilized. Table 1 lists the original shoreline classification used in Bristol Bay and indicates which types would be combined together. The proposed seven shoreline types have broad applicability anywhere in the United States, although oil-retention coefficients may vary (e.g., for northern temperate marshes versus Gulf of Mexico mangroves, which would be classified similarly).

TABLE 1. Percentage of shoreline by type in Bristol Bay and effects of combining shorelines for the proposed model. Original classification is from Michel et al. (1982). Percentage values are rounded to nearest whole number and therefore, in this case, equal over 100 percent. *Not calculated in original report.

Shoreline Types	Percentage	
	Original Classification	Proposed Classification
1) Exposed rocky	3	> 10 (exposed rocky)
2) Wave-cut platform	7	
3) Fine sand	3	> 16 (sand beach)
4) Coarse sand	13	
5) Exposed tidal flat	—*	✓ (tidal flat)
6) Mixed sand/gravel	16	> 21 (gravel beach)
7) Gravel	5	
7A) Exposed tidal flat	—*	✓ (tidal flat)
8) Sheltered rocky	2	2 (sheltered rocky)
8A) Eroding peat scarp	10	10 (eroding peat scarp)
9) Sheltered tidal flat	—*	✓ (tidal flat)
10) Marsh	42	42 (marsh)
Total	101	101

GENERAL DESCRIPTION OF OIL INTERACTIONS

A description of oil interaction and persistence along six of the seven selected shoreline types: exposed and sheltered rocky shores, sand and gravel beaches (described together), tidal flats, and marshes is presented in Gundlach et al. (1985). The seventh environment, eroding peat scarps, is described below.

Eroding peat scarps comprise ten percent of Bristol Bay coastal habitat. Within the adjacent Norton Sound, peat scarps dominate in the Yukon/Kuskokwim delta region. In temperate marsh areas, peat scarps may occur within marshes as along cut banks and exposed bays. Figure 1 indicates four common types of peat scarps (as observed along the Yukon/Kuskokwim delta). Type (A) represents a straight vertical shore as found along an eroding cut bank of a river channel. Type (B) represents an actively and rapidly eroding area where the adjacent tidal flat and the base of the scarp are completely clear of slump blocks and organic debris. Type (C) contains slump blocks along the flat as well as the base of the scarp. Organic debris is common along the base of the scarp. Type (D) represents an area in which the peat or organic base material is somewhat firmer so that a smaller scarp leading onto a sloping peat base is present. The sloping area (composed of peat) is highly grooved.

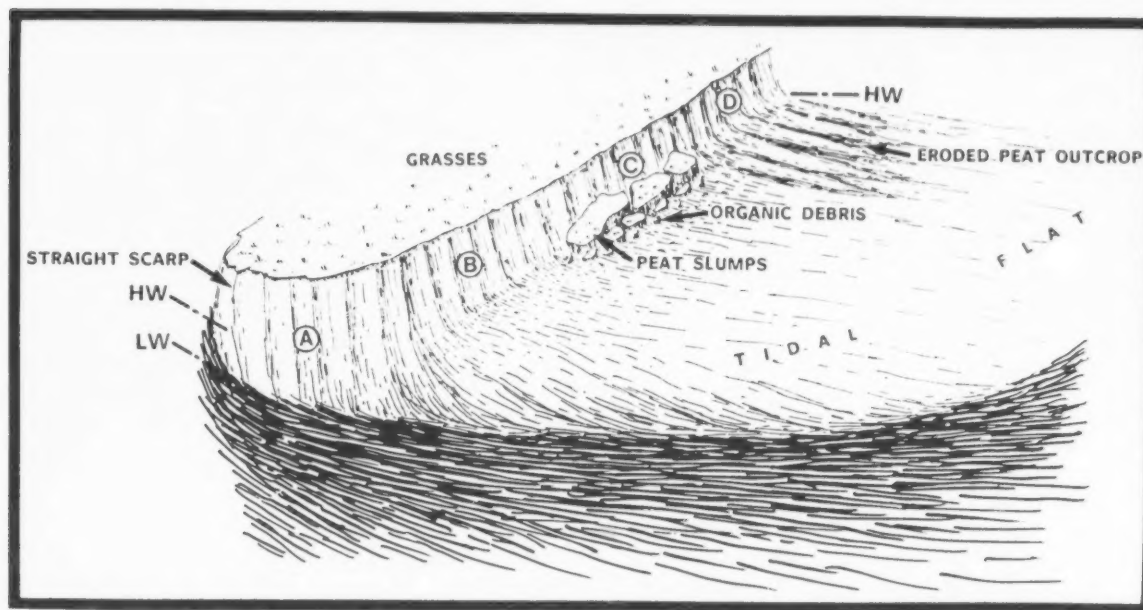


FIGURE 1. Typical eroding peat scarps of the Yukon/Kuskokwim delta.

- Type (A). Vertical scarp as along cutbanks.
- Type (B). Clean scarp leading onto a fine-grained tidal flat.
- Type (C). Slump blocks and organic debris at base of scarp.
- Type (D). Low-lying peat fronting a smaller scarp.

Although eroding peat scarps are a relatively common feature along the coastal environments of the Bering Sea, there is no information concerning their actual interaction with spilled oil. For the purpose of the oil/shoreline model, and until confirmed from field data, the following can be postulated. Basically, oil persistence depends on the erosion rates of the area. Most peat scarps, by definition, are located in actively erosional areas so persistence will be minimal providing that the incoming tide again reaches the oiled zone.

The capability of eroding peat scarp areas to accumulate oil depends on scarp type:

- Type (A) is essentially vertical and similar to a vertical rocky shore with only minimal oil thicknesses capable of accumulating before running off.
- Type (B) is similar but with a concentration of oil remaining at the base of the scarp until washed clean by wave or tidal action.
- Type (C) accumulates more oil in and around the slump blocks and within the resident organic debris.
- Type (D) offers a more gentle slope on which oil might temporarily reside.

Within the Bering Sea, peat bluffs in direct contact with the sea during normal tides are basically unfrozen or contain only small ice lenses. However, along the Beaufort Sea, permafrost bluffs with a large ice content are common (Lewellen, 1970; Cannon and Rawlinson, 1981). Because of its similar form and commonly high erosion rate, permafrost bluffs will be considered equal to vertical peat scarps, at least until additional data are evaluated.

FATE OF BEACHED OIL (ESTIMATION OF OIL-REMOVAL COEFFICIENTS)

After transport by currents, deposition of oil on a shoreline can occur until a certain "shoreline-holding capacity," based on grain size, beach slope, and oil characteristics, is reached. (This will be the subject of a forthcoming paper.) During an ebbing tide, oil has the potential for being deposited on the shoreline. With a rising tide, the newly deposited oil most commonly is again refloated, varying with beach type, degree of mixing with sediments (i.e., causing a density change in the oil), and wave action. Although observational evidence of this occurrence is common, few measurements of the amount of oil removed per day or per tidal cycle are available. Diagrams based on the *Amoco Cadiz* spill are presented in Figures 2 and 3. Figure 2 illustrates oil lifting off of a tidal flat and beach during the first weeks of the spill, but as the oil lost volatility and picked up sediment, less refloating occurred. Figure 3 illustrates oil refloating occurring on a compacted, well-sorted, and water-saturated, fine-sand beach. Refloating over muddy tidal flats is illustrated in Figure 4 (from Allen et al., 1978).

The greatest extent of refloating occurs in cases where a thin layer of water (as in water-saturated sands or muds) lies between the oil and sediment and actual oil contact with sediment is minimal. As this contact increases, as when the beach is dry (upper berms) and coarser grained (coarse sand, gravels, and cobbles), the sheet layer of oil is broken, and oil can adhere to or mix into the sediments, thereby greatly reducing refloating.

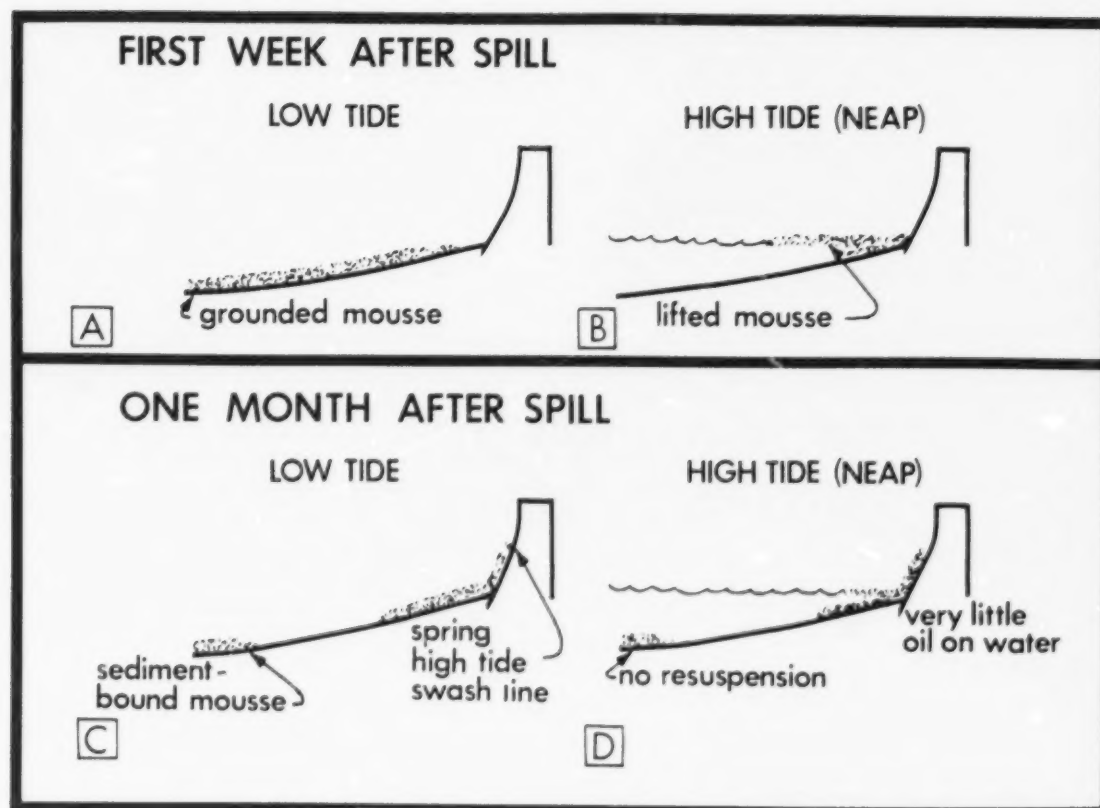


FIGURE 2. Examples of oil on a coarse-sand beach and tidal flat during the *Amoco Cadiz* oil spill. During the first few weeks, most of the oil lifted off the flat with each tide. However, after one month some oil remained on the beach and flat as the oil became bound with the sediment. From Gundlach and Hayes (1978).

Although the general processes of reflotation are fairly well understood, there is only limited data from which to determine the rate at which this occurs. Additional complications may also arise because of unusual climatic conditions, an efficient clean-up operation, minor geomorphic occurrences (e.g., offshore islands causing tombolos where natural oil removal slows markedly), etc. Nevertheless, in order for the oil/shoreline model to work, realistic estimates of oil removal rates are necessary.

Based on personal observations of oil removal and affecting processes at several major spills (Gundlach et al., 1978; Gundlach and Hayes, 1978; Gundlach and Finkelstein, 1981; Gundlach et al., 1979; Gundlach et al., 1981; 1982; 1983) and from the Canadian BIOS study (Woodward-Clyde, 1981), a series of removal coefficients are defined for each of the seven shoreline types that have been previously described. The removal coefficient (K_r) is based on application in a simple, first-order equation that defines the estimated daily rate at which oil will be removed from the shoreline (providing it is in the area wetted by tides; that is, oil is modeled such that if deposited high on the shoreline as during storms, it will be subjected only to chemical and not physical processes.) This equation is as follows:

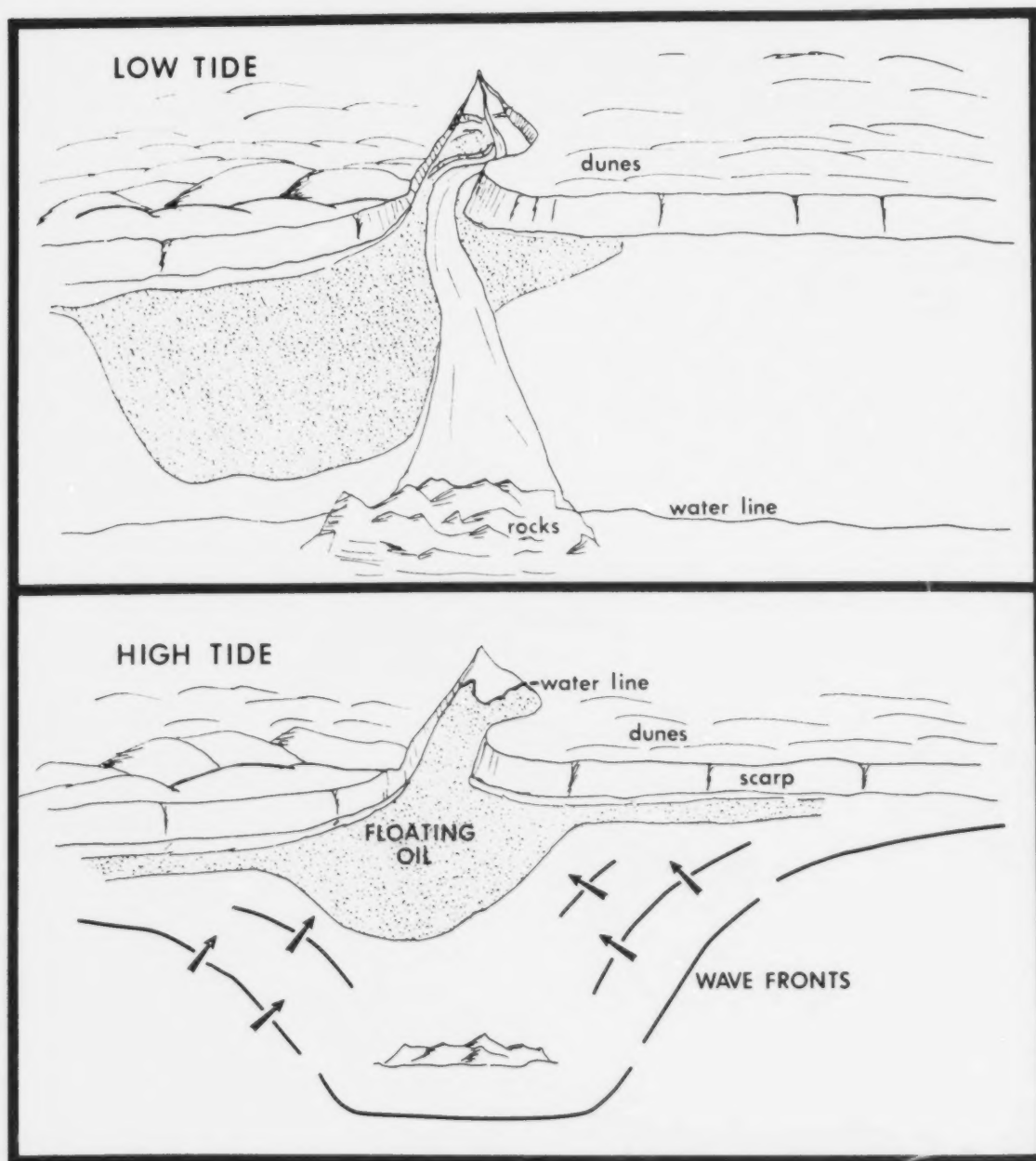


FIGURE 3. Example of oil refloating off a fine-sand beach during the *Amoco Cadiz* oil spill. During flood tide, all oil was lifted off the surface of the fine-sand beach and transported back into the marsh channel. As the tide receded, oil was redeposited on the beach face. From Gundlach and Hayes (1978).

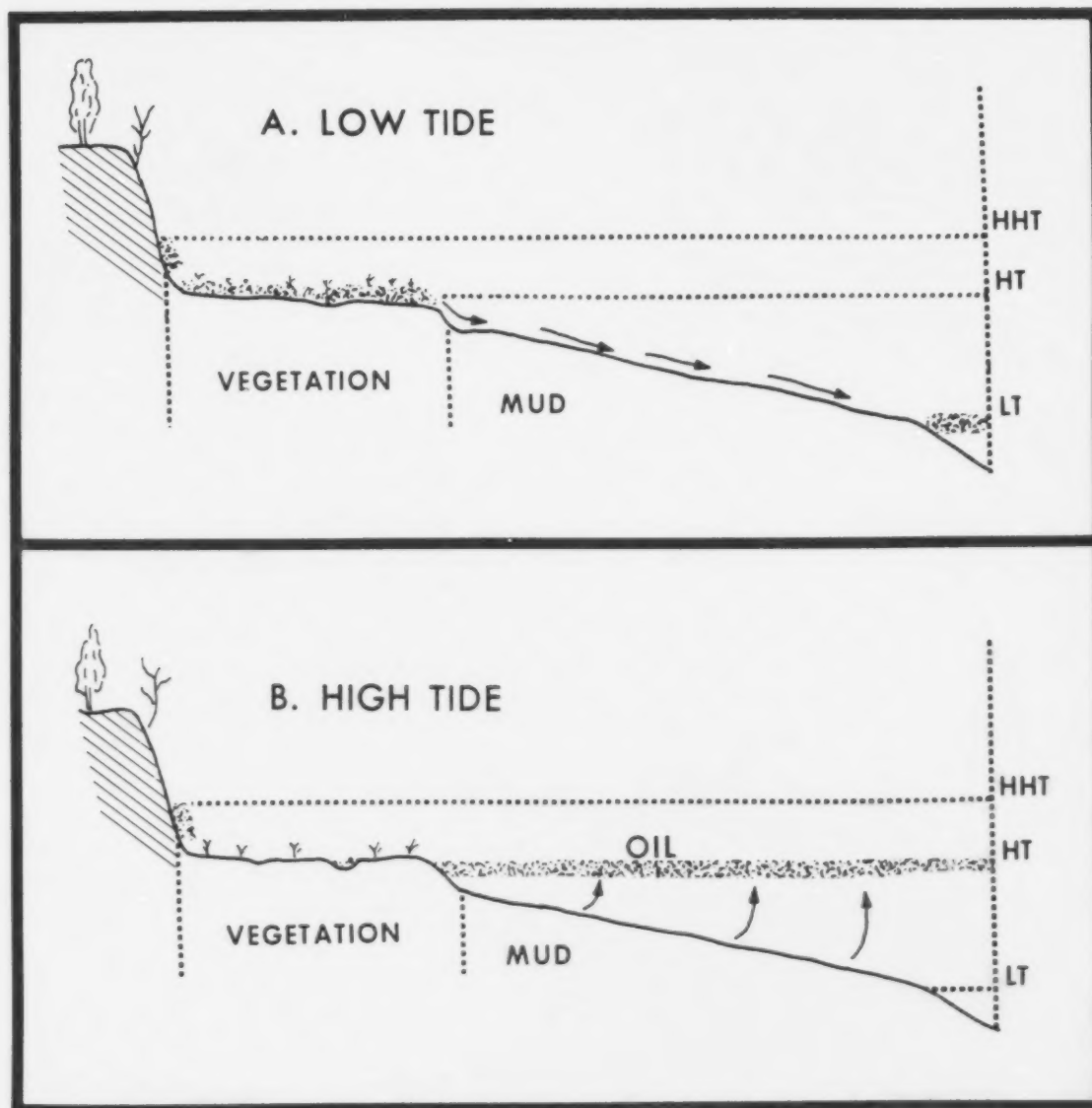


FIGURE 4. Cross-section of oil refloating off a mud-dominated tidal flat during the *Amoco Cadiz* oil spill. From Allen et al. (1978). LT = low-tide level; HT = high-tide level; HHT = high high-tide level.

$$M_i = M_{io} e^{-K_f t} \quad (\text{Eq. 1})$$

- where M_i = mass of oil in beach segment i .
 M_{io} = mass of oil originally deposited on the beach.
 K_f = removal rate constant based on exponential decay to characterize oil loss rate for each beach type.
 t = time in days since original deposition.

Rate constants for all shoreline types are presented in Table 2 and Figure 5. In each case, a range of values is given to reflect some of the variability in oil deposition on coasts and yet maintain a specific internal relationship. As indicated, oil on gravel beaches is harder to remove than from sand beaches due to the greater difficulty in moving gravel-sized sediment. Sand and gravel beach types and eroding peat scarps are further divided by wave energy (<1 m or >1 m waves) to indicate that oil removal greatly increases with higher waves (e.g., twice as rapidly on sand beaches). Sand and gravel beach types are also differentiated into beach face and backbeach compartments to indicate that removal from the backshore is slower than from the beach face. Marshes, by far, show the slowest oil removal rate while tidal flats and exposed rocky shores show the fastest rates.

Of all the beach types indicated in Table 2 and Figure 5, only eroding peat scarps are without supporting evidence (since no published spill reports include this beach type). It is felt that during oil deposition, oil may bind with the organic peat material, thereby greatly inhibiting its removal. Under calm or low wave conditions, this oil is likely to remain adsorbed onto the peat so removal rates are relatively low (i.e., equal to those of a gravel beach, but not as low as a marsh). Under higher waves, defined as having wave heights greater than 1 m, oil removal is quite rapid since the entire scarp is likely to experience erosion under these conditions. Therefore, removal was set as greater than for sand beaches, but not as rapid as for tidal flats. Upon field studies during a "spill-of-opportunity," these rates can be better refined.

The BIOS project in the Canadian arctic, which followed a series of test oil plots for several years, provides a test of the rate curves as presented in Figure 5. In that study, plots were positioned so that approximately 80 percent of the oiled area was below mean high water, 20 percent above. Two adjacent plots along an exposed mixed-sand and gravel coast were rapidly altered by wave-induced erosion, removing most of the oil within two days. In the low wave-energy plots (also mixed sand and gravel), oil was removed comparatively fast by tidal influences alone due to the high groundwater table. A summary of mass balance for the first eight days of the study is presented in Table 3. Note that between 29 and 90 percent of the oil was removed within this time period by wave or tidal action, whether along a sheltered or an exposed beach. Figure 5 compares the BIOS analysis to the projected rate curves for the model, illustrating a relatively good comparison.

TABLE 2. Preliminary daily oil removal rates as a function of shoreline type and wave energy. K_f values reflect the amount of oil remaining within that particular segment of shoreline via application of Equation 1.

Shoreline Type	Characteristics	Percent Removed (1 day)	Percent Removed (5 days)	K_f Value
Rocky Shores				
•Exposed	-Most oil readily lifts off uniform and wetted surface	60-63	99-99.3	0.90-0.99
•Sheltered	-Long-term persistence due to reduced wave energy and rugged substrate	5-10	5-22	0.01-0.05
Eroding	-Basically erosional but oil may adhere to substrate			
Peat	-Under low wave (<1 m) activity	10-18	49-63	0.10-0.20
Scarps	-Under high wave (>1 m) activity	50-55	97-98	0.70-0.80
Sand Beaches	-Mostly surface oiling, but some oil/sand adherence and mixing, particularly with coarse-sand beaches			
	-Generally easy oil removal from beach face, but longer oil persistence along backshore			
	-Under low wave (<1 m) activity:			
	Beach face	18-26	63-78	0.20-0.30
	Backshore	10-18	40-53	0.10-0.15
	-Under high wave (>1 m) activity	40-45	92-95	0.50-0.60
Gravel Beaches	-Mostly surface oil on the beach face, but deep penetration and longer persistence along the backshore			
	-Under low wave (<1 m) activity:			
	Beach face	10-18	40-63	0.10-0.20
	Backshore	5-10	22-40	0.05-0.10
	-Under high wave (>1 m) activity	33-40	86-92	0.40-0.50
Tidal Flats	-Most oil lifts off of wetted tidal flats	60-63	99-99.3	0.90-0.99
Marshes	-Oil tends to adhere to the marsh vegetation and soft, base sediments	0.1-1.0	0.5-5	0.001-0.01

TABLE 3. Estimated oil budget for BIOS study plots after eight days (from Woodward-Clyde Consultants, 1981).

Weathering Process	Percent Oil Removal			
	High Energy		Low Energy	
	Aged	Emulsified	Aged	Emulsified
Atmospheric evaporation	<5.0	<5.0	<5.0	<5.0
Wave action	~50.0	~90.0	<1.0	<1.0
Tidal action	?	?	~29.0	~90.0
Microbial decomposition	<1.0	<1.0	<1.0	<1.0
(Residue)	43.0	0.27	64.0	4.8

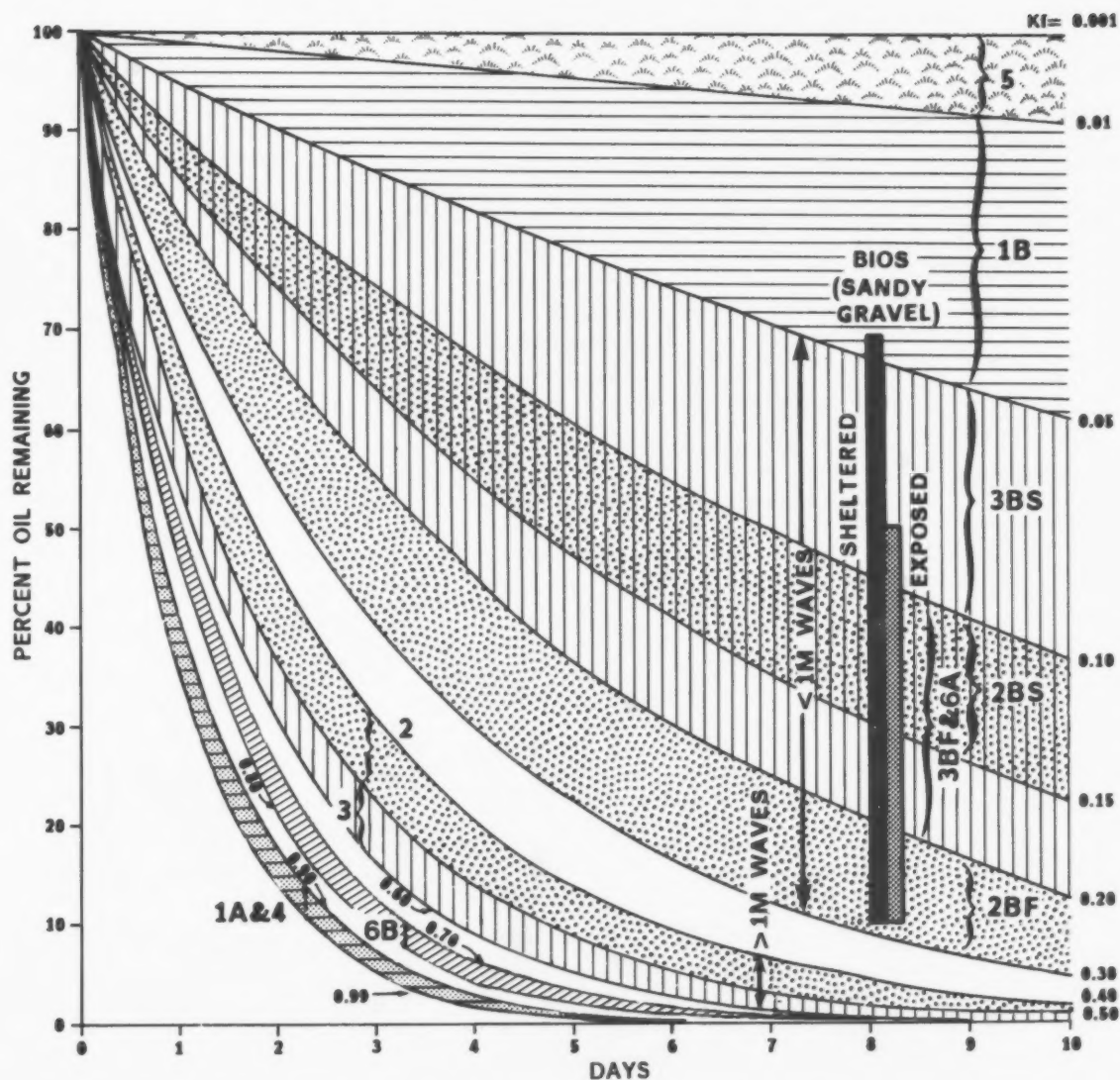


FIGURE 5. Predicted oil remaining as a function of K_f (see Equation 1) and time for different shoreline types:

- | | |
|----------------------------|------------------------|
| 1A = Exposed rocky shore | 6 = Eroding peat scarp |
| 1B = Sheltered rocky shore | A = <1 m waves |
| 2 = Sand beach type | B = >1 m waves |
| 3 = Gravel beach type | BS = Backshore |
| 4 = Tidal flat | BF = Beach face |
| 5 = Marsh | |

Oil remaining after 8 days as measured during the BIOS experiments is also plotted (from Woodward-Lyde, 1981).

FUTURE DEVELOPMENT

Completion of the model is planned for spring 1987. During the interim, new spill-related information may change the presented oil-removal coefficients. For summer 1986, a field study is planned for the Alaska peninsula to determine surf-zone and sediment-transport coefficients and changes in beach slope as a function of wave energy. A third part of the study involves testing of the entire SMEAR model (trajectory, shoreline interaction, chemistry, suspended sediment, and surfzone transport) using *Amoco Cadiz* data.

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**Formulation of a Shoreline/Oil Spill
Interaction Model**

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Introduction

Modeling of oil spill trajectories and fates in the marine environment is now an accepted and often required component of offshore continental shelf oil exploration and development risk analyses. Such modeling efforts typically track a surface slick as far as a coastline and stop. The work described here focuses on the mathematical formulation of a model of oil spill behavior inside the surf zone, including longshore transport and onshore-offshore hydrocarbon distribution. The model will operate independently (stand-alone) or in concert with a set of offshore hydrodynamic and oil spill models developed for the U.S. Minerals Management Service and National Ocean and Atmospheric Administration.

Model Development

Figure 1 shows a conceptual model flow chart. At startup, the study area location and physical properties (bathymetry, topography, sediment sizes, beach slopes, and shoreline types) must be defined. The model then enters the time stepping loop. The first step is to access environmental data describing conditions in the study area at the time of interest. These data include the wind and current fields, air and water temperatures, ice cover and movement, water surface elevation, and suspended particulate matter (SPM) in the water column. When the SMEAR model is used in conjunction with the offshore circulation model, environmental conditions will be supplied by the offshore model. Otherwise, the user must supply mean current and wind patterns. The nearshore wave environment is then computed, followed by the resulting longshore flow and sediment transport rate inside the surf zone. If

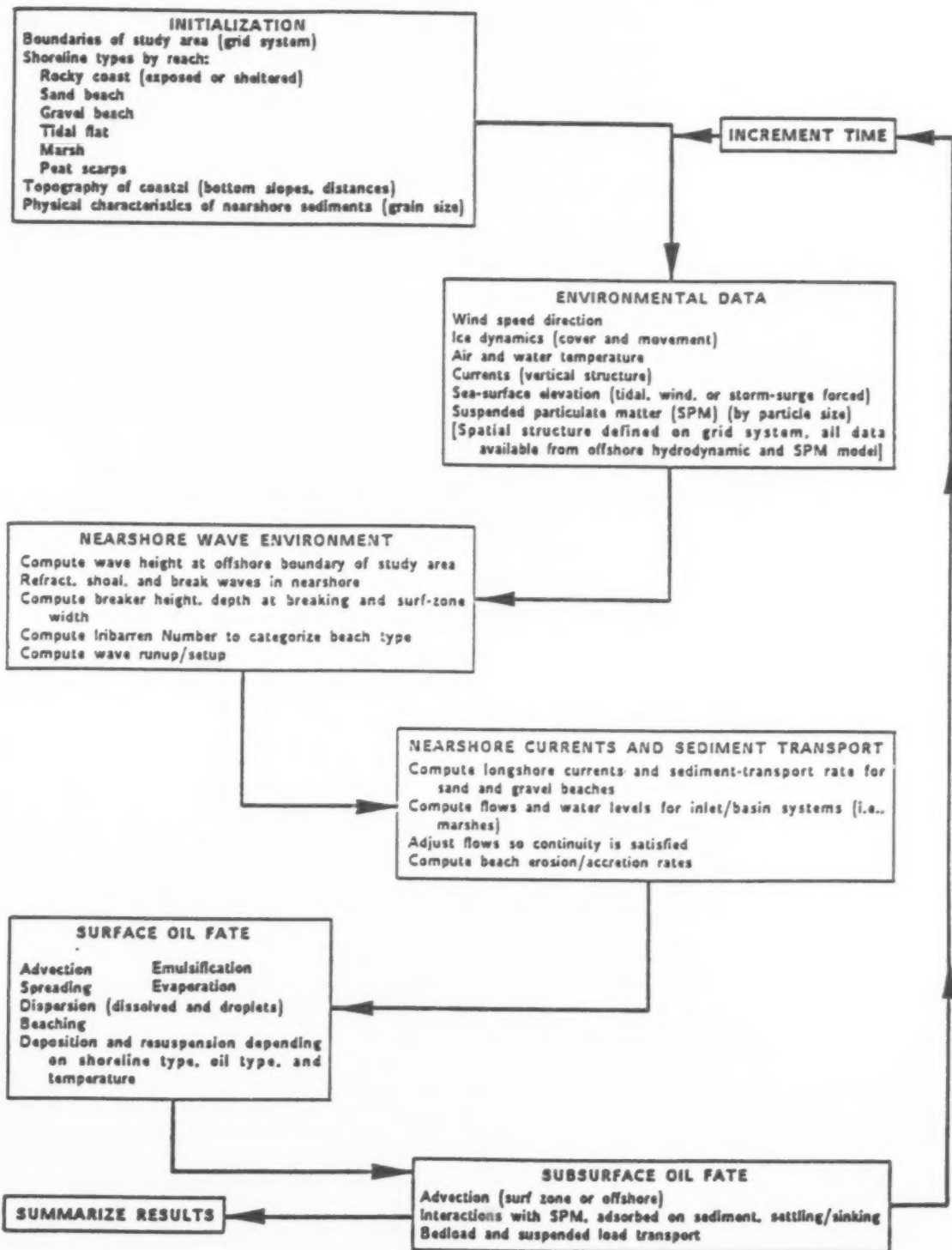


FIGURE 1. Conceptual flowchart for the SMEAR model. [*Input data from offshore wind, hydrodynamic, ice, SPM, and oil model system.]

marsh, lagoonal or tidal flat systems are present, we must estimate the flow into these systems, the change in water level and the area of tidal flats exposed for that stage of the tide. At this point we have a description of the circulation and sediment transport pattern in the nearshore zone.

Now spilled oil may enter the area. Oil is introduced into the study area through one of the model boundaries (likely the offshore boundary), either at the surface or subsurface. The oil continues to weather as appropriate to its location, and is either transported at the surface or in the water column by the alongshore currents. Oil in the water column may adsorb to SPM or be deposited to the sea floor, while oil at the surface may be deposited on the foreshore, backshore, in a marsh or on a tidal flat, or be transported along the shore. The "beached" or deposited oil may be resuspended at later times by changes in sea level, either due to the tide or storm surge. The sequence of steps outlined in Figure 1 is repeated to evolve the spill in space and time. With onshore winds and currents, oil may accumulate onshore until its holding capacity is reached.

At the end of the simulation the spatial distribution of the spilled oil is summarized in terms of the mass of oil deposited in the nearshore, on the surface, or in the water column (either in droplet or SPM associated form). These values are also available at selected time steps of the simulation.

Pooled results of a series of simulations will give a probabilistic description of oil distribution along a coastline. Twenty to thirty distinct weather scenarios will probably be necessary to adequately reflect interannual variability effects on the stochastic distribution of spilled oil (e.g., Samuels and Lanfear, 1983).

Initialization

We have assumed that our interest in oil spill fate and weathering will be focussed on the short term (0-90 days) behavior. This assumption is based on the fact that oil weathering is relatively rapid in the first few days after the spill, and its potential for significant environmental impact decreases as weathering increases. Given this assumption, a study area will typically be on the order of 250-500 km in the alongshore direction and 30-50 km in the offshore direction (Figure 2).

The model is divided into four zones in the onshore-offshore direction: beach, surf zone, and nearshore zone, as shown in Figure 3. Hydrocarbons can enter the nearshore zone (gridded area in Figure 2) either at the surface or in the water column. The processes of dispersion and dissolution control the flux of oil from surface slicks to the water column in both nearshore and surf zones (Figure 3). Buoyancy of oil droplets in the nearshore zone results in a return flux to the surface slick. The model assumes that vertical turbulence in the surf zone results in continuous mixing, overpowering such buoyant effects. The processes of settling and resuspension control the flux of hydrocarbons and SPM between the water column and sediments in both nearshore and surf zones. Oil at the surface in the surf zone can be deposited on the beach. From there it is subject to burial (if the beach is in an accretion stage), or refloating by subsequent tides.

The shoreline is divided into five general classes: rocky cliffs, sandy beach, gravel beach, tidal flats and marshes. This classification scheme allows us to categorize most coastlines in Alaska. Coastline types will typically be specified in length or reach increments on the order of 1-10 km in length. Although one hydrodynamic grid may contain several reach types, no reach may overlay two grids. This simplifies model implementation.

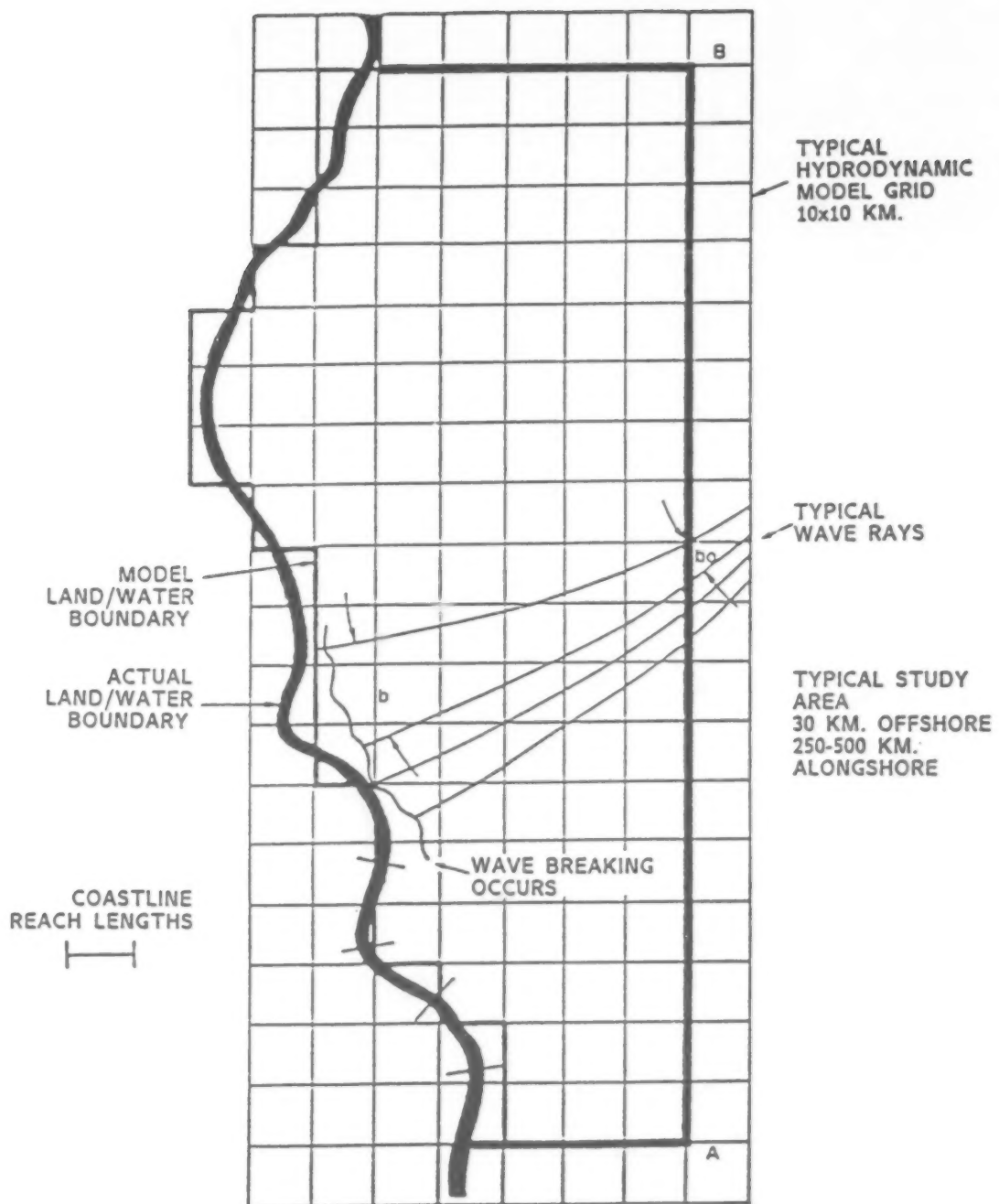


FIGURE 2. Specification of study area and its relationship to the hydrodynamic model grid.

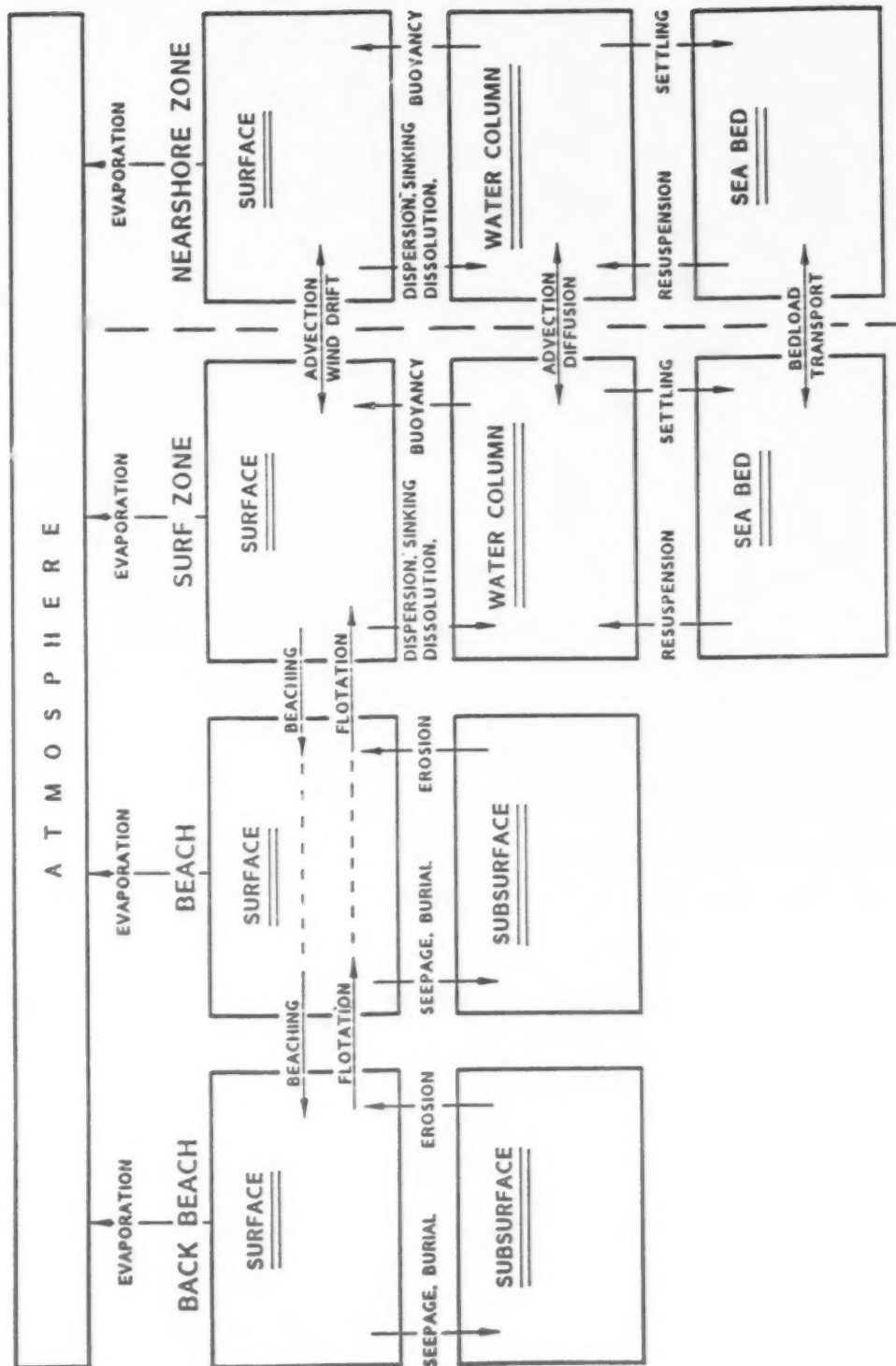


FIGURE 3. Onshore/offshore schematic compartments and dispersion processes for coastal oil-spill distribution model. The dashed line under the surface beach compartment indicates that beaching and flotation may occur directly from the backbeach to the surf zone and vice versa (depending on water levels). Processes associated with aggregation and agglomeration are indicated in "beaching." Oil in the surf-zone water column or on the seabed may beach after passing through the surface component.

The bathymetry of the study area will be derived from the hydrodynamic model grid system for the offshore area. In the nearshore area, detailed local maps and field data (as appropriate) will be used to describe the nearshore topography. To limit the amount of data necessary to describe the nearshore bathymetry, we propose a simple depth, bottom slope system as shown in Figure 4. In this approach all shoreline types can be categorized by three angles, three distances and two depths. In most cases, only a subset of these is needed. The offshore depth h_0 is obtained from the hydrodynamic model bathymetry, hence X_0 is on the order of the grid size for this model. As an example of the use of the approach, if we wish to represent a medium sand beach with a berm, β_{fs} would be set to about 5% slope, and β_{bs} to 2.5%, while X_f and X_b might be 100 m and 40 m, respectively. As another example, if we wish to represent a steep rocky coastline, both β_{fs} and β_{bs} would be set to large values. For a tidal flat, lagoon, or marsh, we specify the number of inlets and basins and the interconnections between them along with the cross sectional areas of the channels and the surface area of the basins. This approach allows enough flexibility to economically represent complex coastal topography. For convenience in the computations, handling of data and accurate representation of the nearshore features, transects will be described perpendicular to the local shoreline in the approximate center of each hydrodynamic model grid.

To characterize sediment type, a simple grain size specification is proposed. A mean sediment size will be used to describe the sediment for each shore segment. The value chosen will be selected to best categorize the sediment transport behavior.

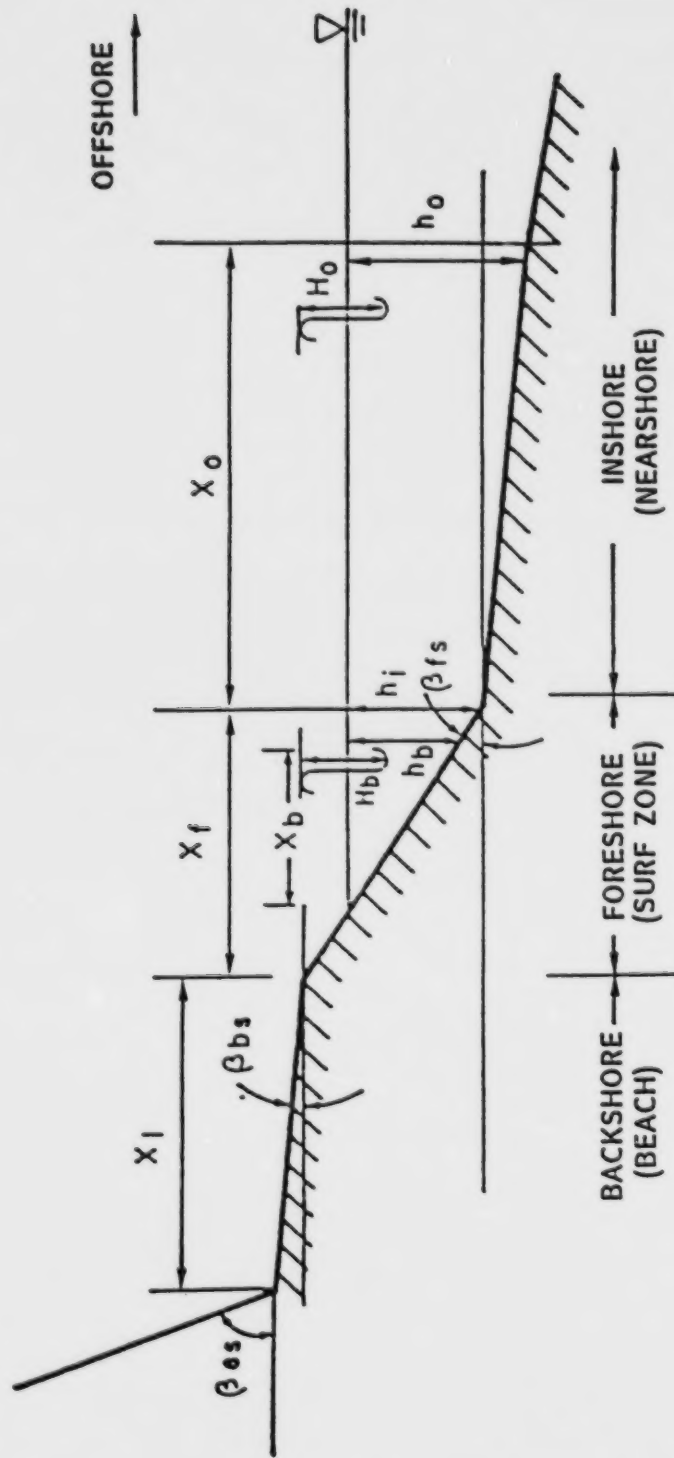


FIGURE 4. Description of nearshore bathymetry.

Environmental Data

Environmental data, including wind speed and direction, ice cover and movement, currents, surface elevation, air and water temperatures and SPM will be provided by the offshore hydrodynamic model system. This data will be provided as a function of time for each grid point within the study area. Secondary variables such as vertical and horizontal eddy viscosities will be averaged over the vertical to parameterize the bulk dispersive behavior.

Nearshore Wave Environment

The wave environment is one of the key parameters in determining the nearshore circulation dynamics. As a first step, the wave conditions along the transect AB (Figure 2, i.e. the offshore boundary of the study area) are determined by using the shallow water wave forecasting equations recommended by the U.S. Army Corp of Engineers Shore Protection Manual (CERC, 1984):

$$\frac{gH}{U^2} = 0.283 \tanh \left[0.530 \left(\frac{gd}{U^2} \right)^{3/4} \right] \tanh \left[\frac{0.00565 \left(\frac{gF}{U^2} \right)^{1/2}}{\tanh \left[0.530 \left(\frac{gd}{U^2} \right)^{3/4} \right]} \right] \quad (1)$$

$$\frac{gT}{U^2} = 7.54 \tanh \left[0.833 \left(\frac{gd}{U^2} \right)^{3/8} \right] \tanh \left[\frac{0.0379 \left(\frac{gF}{U^2} \right)^{1/3}}{\tanh \left[0.833 \left(\frac{gd}{U^2} \right)^{3/8} \right]} \right] \quad (2)$$

$$\frac{gt}{U} = 5.37 \times 10^3 \left(\frac{gT^2}{U} \right)^{1/3} \quad (3)$$

where g is gravity, F is the fetch length, d is mean water depth over the fetch, t is the duration and U is the wind stress factor. U is obtained by estimating the surface wind U_S in m/s from the offshore weather model, and then setting $U = 0.71 U_S^{1.23}$. This approach is used for shallow water waves (i.e. depth to wave length ratio less than 1/2). For depths greater than this, the revised deepwater forecasting equations will be used.

Wind information in terms of speed, direction and duration is determined directly from the offshore weather model. Water depth is obtained from the hydrodynamic model bathymetry. Using a standard refraction/shoaling procedure (CERC, 1984), the wave height, H , at any point can be described in terms of the wave height H_0 at the study domain boundary by

$$\frac{H}{H_0} = \left(\frac{Cg_0}{Cg} \frac{b_0}{b} \right)^{1/2} \quad (4)$$

where b refers to the separation of rays and Cg is the wave group velocity. The subscript 0 refers to the reference location, in this case the offshore boundary, and an unsubscripted variable is at any location.

As the wave progresses shoreward it shoals and refracts as it interacts with the bottom. When the wave-height-to-water-depth ratio reaches an approximate value of 0.73 to 0.78, the wave breaks. This is shown schematically in Figure 2 for the refractive behavior and Figure 4 for the shoaling and breaking response. Knowing the depth at breaking, h_b , and the local slope of the shore, β_{bf} , we can then compute the width and cross sectional area of the surf zone.

To help quantify the various aspects of waves breaking on a plane

beach, such as breaking criterion, breaker type, number of waves in the surf zone, beach type (dissipative vs. reflective), etc. we will employ the surf similiarity parameter or Irribaren number, defined as

$$I_r = \frac{\tan \beta}{(H/L_0)^{1/2}} \quad (5)$$

where β - beach slope

H - wave height

L_0 - deep water wavelength.

Nearshore Currents and Sediment Transport

We next need to estimate the longshore transport velocity V_L in the surf zone. There are a wide variety of formulas available with which to perform this calculation (Komar, 1976; Horikawa, 1978; CERC, 1984; Ippen, 1966). None have been universally accepted. As a relatively simple starting point, some modification of the CERC-recommended formula will be used:

$$V_L = 20.7 \text{ m} (gH_b)^{1/2} \sin 2\alpha_b$$

This formula is valid only for simple sand-gravel beach systems, and hence must be restricted for use in those areas. For areas where tidal flats and marshes are present, the flow is assumed to be in the onshore/offshore direction, depending on the stage of the tide.

A simple inlet basin model (Seelig et al 1977) will be used to estimate the flux into and out of coastal lagoons. This model uses a time-marching method that simultaneously solves the area-averaged momentum equation for the inlet

or breachway and the continuity equation for the bay. At each time step the geometric and hydraulic factors describing the inlet-bay system are calculated by evaluating flow conditions throughout the inlet, and by spatially integrating this information to determine coefficients of the first-order differential equations. This technique can handle any number of interconnected basins and channels, and embayments with large changes in surface area as a function of tidal elevation (i.e. tidal flats). Each channel may further be divided into subchannels to better describe the cross-stream structure of flow within channels.

It is normally assumed in this approach that the pond surface elevations remain horizontal and that the level simply rises or falls. In the present case, the water levels at the offshore end of the channel(s) are described by the offshore hydrodynamic model. A more detailed presentation of the inlet hydraulics model to include governing equations, assumptions and limitations, and comparison to field data for selected inlets, and a user's manual for the computer code are given in Seelig et al (1977).

For steep rocky coastlines we will assume that the hydrodynamic flows predicted by the offshore model dominate, and use those values for any necessary littoral transport.

Given the longshore velocity, which represents the mean velocity over the surf zone, and the cross sectional area of the surf zone, we can calculate the volume/mass flow rates in the nearshore zone.

Calculations of longshore velocity will be performed for each shore segment. Once calculations are made for all segments, minor adjustments of the cross sectional area of the surf zone will be made to assure that water mass is conserved.

Because it is well known that wave runup/setup can transport oil up the

beach face and even into the backshore area, a wave runup/setup calculation will be performed. Since runup on natural beaches is too complex to treat theoretically, we will rely on the numerous laboratory experiments. The graphical procedure outlined in the CERC manual, and illustrated in Figure 6, will be used to make these estimates. The wave set up, η_{setup} is calculated, based on radiation stress concepts, by the formula

$$\eta_{\text{setup}} = K(h_b - h) + \eta_{\text{setdown}}$$

where

h_b - water depth at breaking

h - water depth at point of interest in surf zone

η_{setdown} - wave setdown at the breaker location, given as

$$\eta_{\text{setdown}} = \frac{-H_b^2}{8} \frac{k_b}{\sinh 2k_b h_b}$$

k_b - wave number at breaking

H_b - wave height at breaking

K - a constant, determined by

$$K = \frac{1}{1 + (8/3\delta^2)}$$

where δ is defined by the relation $H = \delta (h + \eta_{\text{setup}})$ in the surf zone, and is frequently taken to be 0.73, the maximum theoretical value of the ratio between wave height and water depth for a solitary wave. By calculating the surf similiarity parameter, we can determine whether setup or runup dominate

for a particular section of beach.

For marsh, tidal flats and rocky cliff coastlines, no runup calculations will be performed since it is not of concern in these areas.

Oil Flux to Study Area

Oil entering the study area will be partitioned into three categories: surface oil, and subsurface oil, free and associated with SPM. The time dependent oil flux across the study area offshore boundary, including its weathered state descriptors, will be provided by the offshore hydrodynamic, SPM and oil models. The surface oil will be described by a series of spillets, each with its own mass, radius, viscosity, density, and weathered state. The subsurface oil will be treated as a number of particles to statistically represent the oil. The "particles" will be described by a range of sizes to represent the range of oil droplet and oiled SPM sizes, and will be distributed to represent the spatial extent of the oil. Given the high turbulence levels in the nearshore area, the subsurface oil will be assumed to be vertically well mixed over the water column.

Surface Oil Fate

The surface oil spillets will be advected by the wind and currents (longshore inside the surf zone, or nearshore outside the surf zone but inside the study area). Spreading, emulsification and evaporation will follow the Fay/Mackay et al (1977; 1980a, b; 1982), Mackay et al (1977) and Payne et al (1981) formulations, respectively. Outside the surf zone, dispersion will be calculated according to Mackay's algorithm, while inside the surf zone this basic approach will be modified to reflect the increased dispersion in this highly turbulent area.

For marsh and tidal flat areas the oil can be transported offshore-onshore into/out of enclosed or semi-enclosed areas depending on the stage of the tide and hence the currents in the inlet/basin system.

We will calculate the beaching of oil due to a change in tidal height by approximating the differential area of the foreshore/backshore exposed during one cycle. If the tide is going out, oil will be deposited according to its thickness, radius, and distance from the shore. If the tide is rising, then some fraction of the oil is resuspended. The amount of oil deposited on or removed from the beach depends on the beach type.

Based on empirical observations discussed in Gundlach et al (1986), oiling on the beach face will average 18 mm for sand, and 9 mm for a medium/coarse sand or gravel beach. Variability will be reflected by probability density functions fit to the data. For a sand beach, an average of 90% of the oil deposited on ebb is removed on the flood tide, while only 70% is removed for a gravel beach.

To estimate oiling in the backshore, we calculate runup as described above. If the oil reaches the backshore area for a sand beach, we assume that oil penetration of the sediment averages 5 cm in depth. The impacted volume per unit shoreline length is then the uprush zone times the penetration depth. Oiled sediment cannot exceed 9% of this volume per unit length. This gives an average holding capacity for this area. For a gravel beach type the depth of penetration is 18 cm. The amount oiled remains the same at 9%.

Oil can be removed from this backshore area during the next high tide, with removal rates of 50% per cycle, provided the wave heights are approximately 1 m or larger.

If oil is incorporated in a marsh, the holding capacity is a maximum of 30

kg/m², or 30 mm surface oil thickness, for marsh that is partially submerged at high tide, to roughly 10 kg/m² for a marsh that is fully submerged at high tide. Of the oil that is deposited in a marsh at high tide, 1% is removed on the ebb.

Oil deposited on tidal flats is assumed not to exceed 6 mm in thickness. Removal rates due to refloitation during the flood tide are assumed to be 99%, given that the oil can generally not penetrate the hard packed sediments that make up most tidal flat areas.

In summary, the loss of oil from the beach is calculated by assuming a simple exponential decay relationship:

$$M_i = M_{i0} e^{-K_f t}$$

where

M_i - mass of oil in beach segment i

M_{i0} - mass of oil originally deposited on the beach

K_f - exponential decay constant to characterize oil loss rate for each beach type

t - time in days since original deposition

Based on an analysis of the field observations (Section 3) of oil-beach interaction we propose the values of K_f given in Table 1. As our model becomes more refined it may be desirable to make K_f a function of the local wave environment, oil viscosity, and beach sediment type. This additional sophistication does not appear warranted at this time.

Oil that is deposited on tidal flats, in a marsh, or on the foreshore or backshore of a beach is assumed to continue weathering due to evaporation. No other weathering processes are active, although biodegradation and photo-oxidation can be added at a later date.

To handle the numerous deposition-resuspension cycles of oil, we propose

Table 1. Exponential removal factor range by beach type

<u>K_f (per day)</u>	<u>Shoreline Type</u>	<u>Characteristic</u>
0.99 - 0.9	1) Rocky shores	Most oil readily lifts off uniform and wetted rocks
0.3 - 0.2	2a) Sand beach faces	Oil readily lifts off fine-sand beaches but partially adheres to coarse sand
0.1-0.5	2b) Sand beach backshore	Oil on sand beaches may be placed far behind the active intertidal zone. K _f varies with wave height.
0.2 - 0.1	3a) Gravel beach faces	Oil partially lifts off mixed fine-sand and gravel beaches but is inhibited in gravels and cobbles
0.05 - 0.4	3b) Gravel beach backshore	Gravels are more difficult to move than sand under swash and low wave activity, and oil tends to be buried deeper
0.99 - 0.9	4) Tidal flats	Most oil lifts off of wetted tidal flats
0.01 - 0.001	5) Marshes	Oil tends to adhere to the marsh vegetation and soft base sediments

to break the surface slick into sub-lots. As the tide recedes, a sub-lot of a surface spilllet is deposited on the shore. Some portion of this sub-lot may be resuspended later (i.e. during high tide) or remain deposited on the shore or in the marsh. As the sub-lots are resuspended, they will be incorporated into existing spilllets, using a weighted mass balance by hydrocarbon cut, for transport and dispersion calculations. This procedure should minimize the computational time/storage, but give a relatively accurate representation of the spatial and temporal distribution of the oil.

Subsurface Oil Fate

Oil in the water column is described by particles that statistically represent oil droplets. There are generally two classes of particles, oiled SPM and free oil particles. Since the quantity of dissolved oil is usually much smaller than that in droplet form, we will lump the dissolved and droplet oil into one category. These particles will be advected according to the local current field (longshore currents if inside the surf zone, and hydrodynamic modeled currents outside the surf zone but within the study area), and dispersed by a random walk diffusion procedure (Csanady, 1973). The effective dispersion coefficients will be derived from the hydrodynamic model. Settling of the oiled SPM particles will be performed using a Stokes fall velocity.

The SPM oil interaction will follow the work currently in progress by Payne et al (personal communication) at SAI under MMS sponsorship. The oil adsorbed onto sediment is calculated by

$$C_{\text{adsorbed}} = K f_i S_i C_{\text{total}}$$

where K - dimensionless partition coefficient $\times 10^3$

S_i - SPM concentration

$C_{total} = C_{adsorbed} + C_{dissolved} + C_{entrained}$

Estimates of the concentration of oiled SPM and free droplets of oil can be obtained by dividing the mass of the oiled particles or oil in each grid by the grid volume. This is a relatively coarse estimate, but is probably sufficient for the analysis at hand.

Through this calculation sequence we can advect and disperse oil droplets and oiled SPM in the nearshore zone. If the fall velocities are sufficiently large, oiled SPM will be deposited on the sea floor, and either transported as bed load or buried.

Outside the surf zone, estimates of the SPM concentration will be obtained from the offshore model. Inside the surf zone, suspended sediment concentration will be assumed to be a fixed percentage (e.g. 15%) of the amount of sediment in longshore transport, or calculated by the Bijker procedure.

At this point we have completed one time step in the SMEAR model simulation. We anticipate a time step on the order of 3 to 6 hours with total simulation times on the order of 30 days. As time is incremented the calculation procedure is repeated to describe the spatial and temporal distribution of oil in the nearshore area.

At selected time steps, model output will be provided to describe the spatial distribution of spilled oil:

- (1) Oil mass, thickness, weathered state and location (surface, buried) within each coastal segment.
- (2) Location, mass, weathered state, thickness and areal extent of each surface spill.

- (3) Concentration of oiled SPM, SPM and droplet oil in water column.
Mass of droplet oil and oiled SPM at the sea bed.

In addition, complete descriptions of the wind, wave, current, and sediment transport rates are also provided. At the end of the simulation, a mass balance is provided describing the distribution of oil in the major environmental compartments: land, water column (oil and oiled SPM), sea bed, atmosphere, and sea surface.

The model as presented above is essentially a deterministic calculation in that it follows the fate of a specific spill through a prescribed set of environmental conditions. To run the model in a probabilistic mode, repeated simulations of the deterministic model will be performed. The environmental conditions and the model parameters used to describe the oil spill transport and fate necessary as input to the model will be selected using probability distributions appropriate to each parameter. For instance, the wind speed and direction could be randomly selected from historical records for a particular season. As another example, the oil content by volume of oily beach sediments could be selected by assuming a simple Gaussian distribution of the values.

After multiple simulations have been performed, the results will be aggregated to determine the probability of a given amount of oil in each segment as a function of time since the spill entered the SMEAR model boundaries. Note that this probability distribution is for a given spill event. The exact number of simulations necessary to reliably define the probability distributions is not known at this time but will be empirically determined once the SMEAR model is in operation. We expect that 20-30 simulations will be required to adequately reflect interannual variability in the results (Samuels and Lanfear, 1983). The user may opt to investigate other oil-spill scenarios

by simply repeating the above calculations using the described spill characteristics.

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THE DISPERSION AND SUBMERGENCE OF OIL SPILLS

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ABSTRACT

Some results are presented and discussed from two research projects concerning the behaviour of oil spills on ocean surfaces. First is a study of aspects of the process of chemical dispersion of oil spills in which an attempt has been made to observe and quantify the fundamental processes which occur when droplets of dispersant land on an oil slick and induce dispersion. Second is a study of the factors which result in an oil slick breaking up into discrete droplets on the ocean surface (as distinct from remaining as a continuous slick), how these droplets may coalesce to form larger oil pans or pancakes, and how these droplets and pans of various sizes tend to become submerged (or apparently submerged) and thus invisible to the eye or to remote sensing systems.

INTRODUCTION

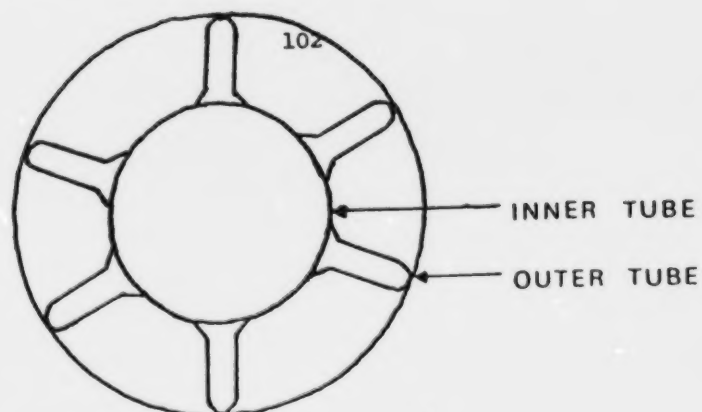
In previous AMOP presentations in 1984 and 1985 we described an experimental system termed the "double tube" or "Bobra" apparatus (Bobra et al., 1984) in which it is possible to observe the dispersion process at close proximity from above and below. Measurements can also be made of the extent of chemical dispersion. In a previous report (Mackay, 1985 and Mackay et al., 1985) we postulated a two regime dispersion model in which the extent of dispersion was controlled for relatively thick slicks by the performance of the dispersant and for relatively thin slicks by the accessibility of the oil to the dispersant drops. In this study we have used this system to observe and measure the dispersion process in the hope of shedding further light on the mechanism and thus effectiveness of this countermeasure.

In another report (Wilson et al., 1985 and Mackay, 1985b) we studied the process of oil droplet submergence in a stratified water column in an attempt to explain the anecdotal reports that large quantities of oil sank and drifted sub-surface to shore. We noted that an oil pan floating in water was often "overwashed" with water and appeared to be submerged, especially if its density approached that of water. We have studied this phenomenon in more detail using various systems including variable density wood blocks, pans of lard and plastic balls, and have attempted to assemble a mathematical model or treatment of the submergence phenomena. As part of this study we have also sought to determine why certain oils tend to form oil "pans" or "pancakes" or "rafts" whereas other oils remain as a slick or disperse into small droplets. This has involved a series of experiments with different oils subjected to prolonged turbulence on the water surface. Observations were made of the changing conditions of the oil.

Dispersion Tests

As shown in Figure 1 the apparatus consists of a 5.4 cm inner diameter by 19 cm high glass tube fitted into a 9.2 cm inner diameter by 29 cm high glass

TOP VIEW:



SIDE VIEW:

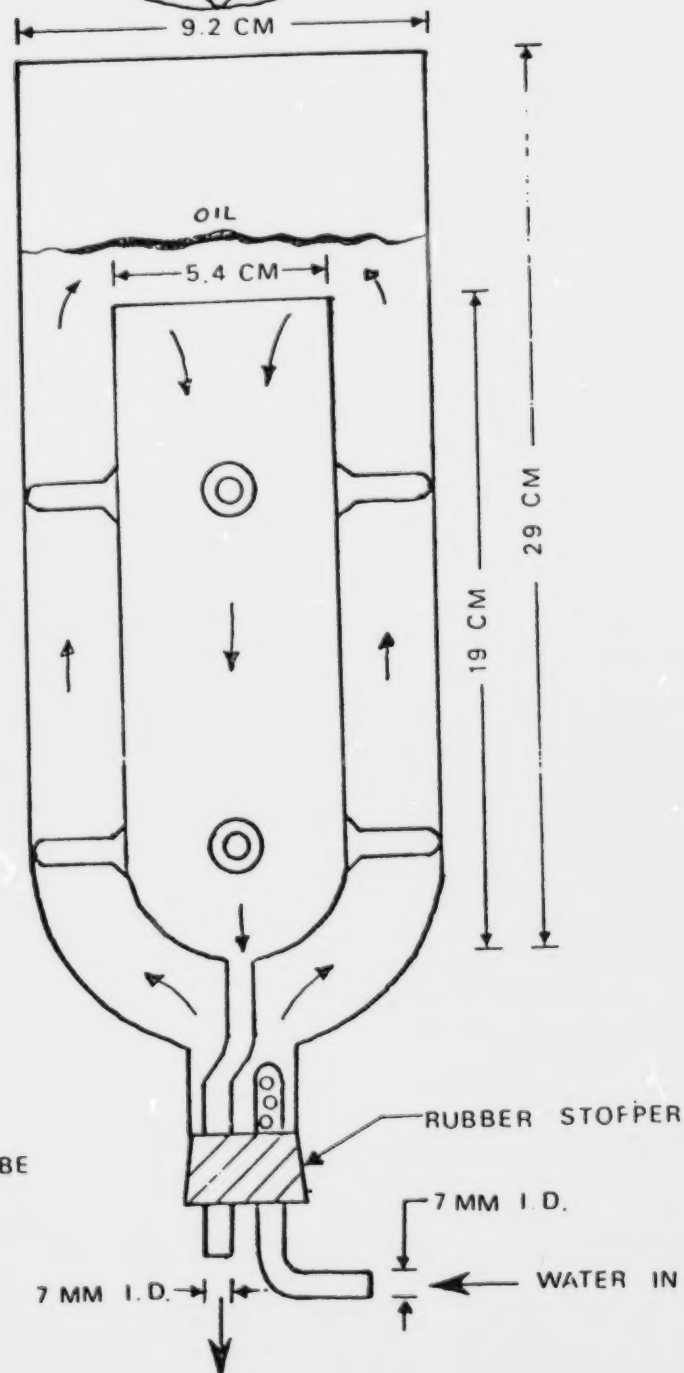


Figure 1:
DOUBLE TUBE
APPARATUS

tube. Six radial glass supports on the inner tube ensure that it remains centred within the larger tube and stable during flow. Both tubes were tapered at the lower end. The inner tube is connected to a 7 mm inner diameter tube and the outer tube to a 2.5 cm inner diameter opening. This opening is sealed with a rubber stopper with one hole to accommodate the 7 mm tube of the inner tube and the other to accommodate another 77 mm inner diameter glass tube which is sealed at the end and is perforated with small holes to allow the flow of water into the apparatus to be evenly distributed. This results in a uniform flow of water between the two tubes, and to the inner tube.

The apparatus is connected to a constant level tank with Tygon tubing. Valves controlled the water flowrates in and out of the apparatus and allowed the water level in the apparatus to be regulated.

For a typical dispersion test, a steady flow of water (salinity 33 g/L) at 2.5 L/min was started through the double tube apparatus, and the water level was set at 0.5 to 1.0 cm above the top of the inner tube. A known volume of oil was added to the water surface from an appropriate pipette. The dispersant was then added, regulating the drop size to the oil surface from a syringe with the tip located at a height of 1 to 2 cm above the slick.

To measure the amount of oil dispersed, the inlet and outlet flow of water were clamped shut and the oil was allowed to settle for 2 minutes. A known mass of 2.5 cm-square oil 3M sorbent was placed on oil/water surface to soak up the oil. The sorbent was then weighed to determine the amount of oil remaining and dispersed. Allowance was made for the amount of water absorbed by the sorbent.

To assist in interpreting the data obtained, two series of photographic records were obtained of the dispersion process.

In February 1986 a series of dispersion tests was conducted at the University of Alberta with the assistance of Drs. Peter Smy and Dick Hales. The system used was a Motion Analysis System Model SP 2000 consisting of a camera with a solid state image sensor capable of scanning at a high rate of frames per second. In this work a speed of 200 frames per second was used. The image was processed and stored on video tape.

Three oils were tested, EPS Standard, Sable Island Crude Oil and Arabian Heavy Crude Oil. The dispersants used were Corexit 9527 and BP MA 700. Density and viscosity data are given in Table 1.

Table 1: Density and Viscosity of Oil at Room Temperature.

Crude	Density (g/mL)	Viscosity (mPa.s)
EPS	0.8360	4.8
Sable Island	0.8420	2.4
Arabian Heavy	0.8950	64.4

Some additional conventional cine and still photography was conducted at the University of Toronto using a Kodavision Series 2000 8 mm video camera and an Olympus OMI camera fitted with a motor drive.

The photography showed that after the dispersant drops landed on the oil surface there was a delay of some seconds as penetration and some mixing occurred. After the dispersant reached the water surface it caused a sudden rupture of the interface and rapid herding. Presumably the total water-

dispersant-air interfacial energy is less than the water-oil-air energy. Dispersant drops were observed to enter the water column and sink. Regions of oil-water interface were observed to be unstable and subject to emulsification, especially when agitated. Presumably the oil-water interfacial energy or tension becomes very low and resistance to deformation is negligible.

The University of Alberta results were stored on video tape and have been supplied to the scientific authority. Since the record is black and white it is often difficult to discriminate between dispersant and oil. A colour record is preferable. Nevertheless, valuable pictures of the dispersion process were obtained. The dispersion process may take a total of one minute thus very high speed recording can result in prolonged viewing times. The ideal recording speed is probably about 60 to 90 frames per second. Rapid motor-driven still photography with a 35 mm camera is even feasible because it gives a very clear print.

The times necessary for the dispersant drop to penetrate through the oil layer and reach the water surface are given below in Table 2.

Table 2: Time (seconds) for the Dispersant to Sink Through the Oil Phase to the Oil-Water Interface.

Oil	Slick Thickness (mm)	Corexit - 9527	BP - MA700
EPS	0.45	1.92	2.69
	0.75	5.72	---
	1.50	2.30	1.30
Sable Island	0.75	0.5	0.5
Arabian Heavy	0.45	19.7	20.7
	0.75	25.98	22.21
	1.5	25.6	22.20

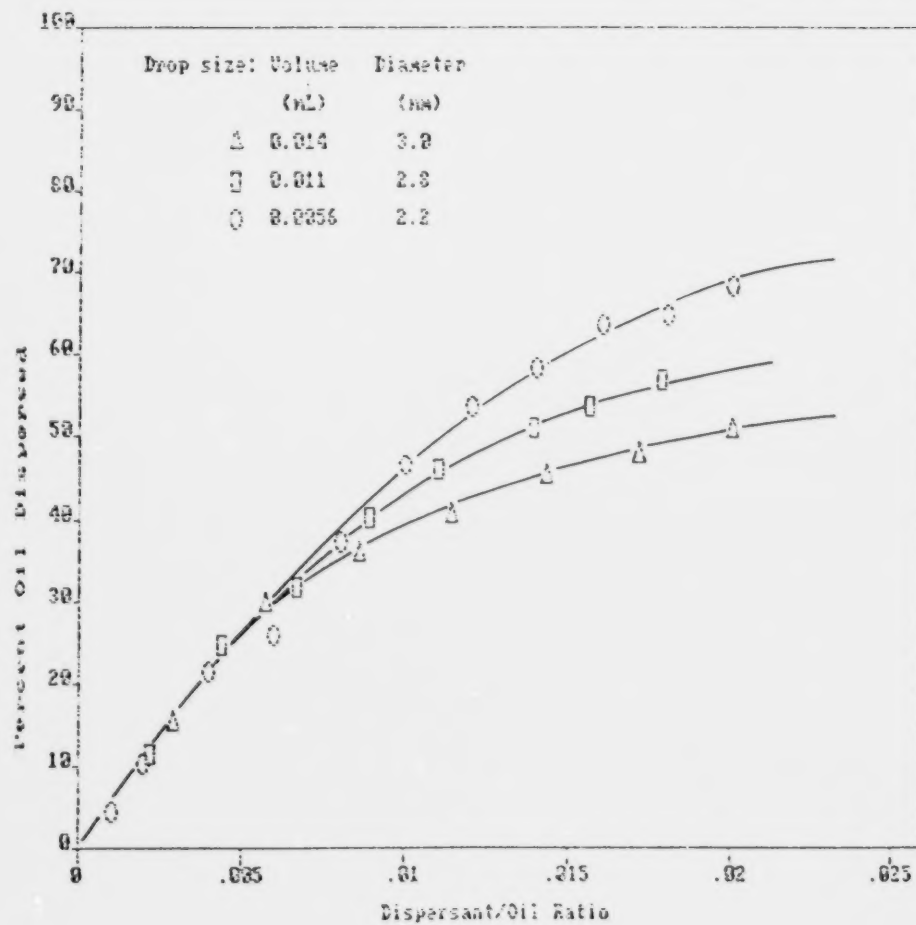
These results indicate that oil viscosity is the key determinant of sinking time. A 1 mm slick of these three oils will experience a time of approximately:

EPS:	3 seconds	Viscosity: 4.8 m.Pa.s
Sable Island:	1 second	Viscosity: 2.4 m.Pa.s
Arabian Heavy:	25 seconds	Viscosity: 64 m.Pa.s

Thus it appears that the time for penetration of a 1 mm slick (in seconds) is approximately twice the viscosity (in mPa.s). An implication is that for very viscous oil slicks, eg. 1000 or 10000 mPa.s or centipoise, the penetration time may be many minutes or even hours. During that time there is a possibility that the dispersant may be washed off the oil. It is suspected that oils may form a "skin" adjacent to the water interface which will further impede migration of surfactant to the interface.

It is believed that dispersant drop diameter has an effect on dispersing efficiency (Mackay *et al.*, 1985). To investigate this a series of tests was conducted varying the drop volume from 0.0056 to 0.011 to 0.014 mL i.e. from 2.2 to 2.8 to 3.0 mm diameter. The results are given in Figure 2.

Figure 2: Effect of dispersant drop size on dispersion



Initial oil slick thickness 0.75 mm dispersant oil
 Corexit 9597
 Oil- EPS standard

In the early range when less than 30% of the oil slick was dispersed there was no effect of dispersant drop size. At higher percentages, i.e. when the slick became thinner than 0.30 mm there was a definite effect for a larger number of smaller drops to be more effective. But in this second regime the slopes of the lines decrease and the dispersant is clearly less efficient.

In the early regime each volume of dispersant is dispersing approximately 50 volumes of oil, but this ratio drops to about 20 at higher dispersant amounts. This behavior is consistent with the "performance" and "access" regimes discussed by Mackay *et al.*, (1985).

These results are consistent with a situation in which each drop of dispersant is able to disperse approximately 50 times its volume of oil until the oil slick thins to the point that the volume of oil which is to be accessed extends over an area of diameter 10 to 12 times the drop diameter. As the slick thins the volume dispersed per drop falls in a first order manner. This diameter factor (here 10 to 12) was described earlier by Mackay *et al.*, (1985), a value of 5 being used to fit data from a variety of experimental slicks.

It should be noted that these dispersant drops are large compared to the drops which would be generated by a dispersant-spraying aircraft, i.e. 3 mm vs. 0.4 mm. It would be useful to devise a method of generating smaller drops for application to laboratory oil slicks. The most attractive approach appears to be the use of a motor-driver syringe pump delivering a dispersant flow into a nebulizing nozzle with controlled air flow. The air flow is necessary to generate the shearing action to remove the drops from the syringe source before it reaches the size of a few mm necessary for gravitational disengagement.

In conclusion this study has shown that the double-tube system is convenient for both viewing the dispersion process and for determining the effectiveness of dispersants. A clearer picture has emerged of the dispersion process, but it is believed that further work is justified, especially using smaller diameter dispersant drops.

The results tend to confirm the existence of two dispersing regimes with a transition occurring at a particular oil slick thickness.

PAN FORMATION TESTS

Ten experiments were performed in a glass walled tank 120 cm deep by 47 cm square with an oscillating hoop agitation system.

In the experiments a known volume of crude oil or crude oil mixture was added to the fresh water surface and oscillation started. Visual and photographic observations were made at various times to monitor the condition of the oil. Oil samples were taken periodically for analysis by gas chromatography. At the end of the test, which varied from 2 to 7 days, the oil was recovered and its density, water content and composition were measured. The oils studied were principally weathered EPS Standard oil and mixtures of that oil with various other hydrocarbon components which are believed to influence pan formation.

It was observed that the oil slick went through a series of fairly distinct stages. Initially it was present as a slick of variable thickness with areas of sheen and thicker areas. As the slick aged the oil tended to gather into "rafts" of fairly thick oil surrounded by water. This seemed to be due to a reduced spreading tendency and a higher oil density and viscosity. Later the oil tended to break up into "blobs" of oil which were several mm to several cm in diameter and showed a reduced tendency to coalesce with each other and with the raft. The blobs were almost always awash with water or

fully submerged thus they could not easily be seen from above the water surface. They later turned lighter in colour to a light brown "mousse" containing some 60% water. Also formed, especially initially, were oil-in-water emulsion particles and oil coated water drops, i.e. water in oil in water drops or "balloons" of oil in water.

The oil blobs retained their near spherical shape as long as conditions were turbulent, but if they were allowed to rest on a stagnant water surface they tended to spread out. The emulsified blobs on the other hand retained their shape.

Tests were conducted with an oil doped with wax and with asphaltenes and surprisingly this had relatively little effect apart from increasing the oil's viscosity and generally slowing down the overall process of change from slick to raft to blob. When the slick was subjected to UV light there was more rapid formation of emulsion indicating that surface-active photo-products were formed and played a role in the changing interfacial properties of the oil.

The full implications of these results have not yet been assessed but it appears that as an oil weathers on a turbulent water surface it passes through several regimes which are controlled by oil density, viscosity, interfacial characteristics and the possible formation of a "skin" of relatively viscous material which resists deformation and coalescence. This "skin" formation may be enhanced by photolysis. What remains unclear is how the water in oil emulsion forms. It may result from the coalescence of blobs with only a partial "skin", insufficient to prevent coalescence, but sufficient to stabilize the small water drops which are formed from the imperfectly drained water film which exists at the coalescing surface.

What is needed is a comprehensive analysis of the oil's physical and chemical properties as it progresses through the various regimes, supplemented by carefully designed experiments to test the emerging hypotheses.

In terms of oil slick behaviour it appears that oils which are slow to disperse or emulsify to form oil in water emulsions or fine droplets may survive long enough to lose their ability to disperse, thus passing at least in part into a sequence of regimes in which they form "rafts", "blobs", mousse and eventually tar balls. Just what combination of properties corresponds to this loss of natural dispersing ability is not yet known but it seems to be a combination of viscosity and interfacial or skin stability properties. It is clear that when an oil forms blobs it will be substantially submerged and not necessarily readily visible from the surface. The blobs may remain a few cm in size or they may coalesce to form larger masses or pans which continue to weather and retain their integrity eventually weathering into tar balls.

SUBMERGENCE STUDY

Initially it was proposed to construct "oil pans" of variable size and density from wood, hollowed out to accept ballast, and study their behaviour both tethered and free-flowing in a wind wave tank. Maximum raft width was constrained by the width of the available wind-wave tank to 60 cm. The degree of submergence was to be measured optically by determining the absorption of light between the raft and the surface by dyed water. Three approaches were envisaged.

- (a) Illumination from above, reflection at the raft, then sensing from above.
- (b) Illumination from a light source within the raft and sensing above.
- (c) Direct video photography from above with calibration.

Method (a) has the disadvantage that some light is reflected from the water surface, but it is very simple. Method (b) is more reliable but requires a light source in the raft. Method (c) is less quantitative but it gives a good, direct picture of the raft including time and position variations in water thickness over the raft.

Results were obtained using system (a) but a number of problems became apparent. The signal changes rapidly as waves wash over the surface, as reflection occurs at the water surface, and as the pan tilts. It is difficult to conduct the experiments with a free-flowing untethered pan. It was also time-consuming to construct a large number of pans.

Accordingly it was decided to investigate system (c) i.e. the use of direct video photography using various densities and sizes of pans in an untethered condition. It was impractical to use actual oil pans, thus a simulated material was sought. Some effort was devoted to the use of gelled mixtures of water and an alcohol such as methanol or ethanol which could be made up to the required density. A dye could also be added to enhance visibility. Suitable cross linking gelling polymers were obtained and some success was achieved but it became clear that the development of a recipe for the preparation of plastic gelled pans of a variety of properties and sizes was a study in itself requiring more time than was available. A simple solution was to make pans out of lard (used in domestic cooking) contained in heat-sealed plastic bags with no air space. These pans could be made in almost any size or shape greater than a few centimetres. Density could be increased by adding lead weights or another suitable ballast material such as sand. This approach has the additional advantage that lard is not an environmentally noxious substance thus there should be little concern with its use in field trials.

For smaller particles, plastic spheres of high density polyethylene were purchased and used directly, or in some cases weighted by gluing sand to their surface.

It was thus possible to investigate the submergence behaviour of a variety of sizes of pans of varying density with a view to establishing quantities such as average or maximum depth of submergence, or time of submergence.

The experimental conditions investigated were fresh water at 18 to 20°C, wind speeds ranging from 0 to 13.5 m/s (with most work being done at 5 m/s) and waves generated by an oscillating paddle at 1.4 Hz to give a wave height of 15-20 cm. The pans and plastic balls were photographed by a Kodak Comcorder 2000 and observed by the naked eye. Direct visual observation proved to be the most satisfactory method.

A series of results was obtained with all systems. It should be emphasized that this is an exploratory study in that it was not entirely clear at the outset what quantitative results could be obtained or how they should be processed or modelled. The following is a brief synopsis of the more significant results.

First, it was desired to determine if overwashing occurred, and if so, what the approximate mean overwash depth was as a function of hydrodynamic conditions. It was found that overwashing did occur, often to a depth of several centimetres. There was; however, a considerable variation in depth with position and time. Further the upper pan surface rarely drained completely of water, thus there was almost always a layer of water of depth approximately 1 mm on the surface.

For example the data from the lard pans at 5 m/s wind speed it was observed that they were submerged virtually all the time with an occasional 20

to 25% of the surface exposed to the air but wetted with water. An approximate correlation of mean water depth S cm was

$$S = 0.009 U^2 / \Delta \rho^{0.8}$$

where U is wind speed (m/s) and $\Delta \rho$ is density difference between water and the pan (g/cm^3).

The pans were also subject to events which were termed "deep episodes" especially when the pan was impacted by a breaking wave. During a typical deep episode the pan would submerge for 5-15 s and reach a depth of 15 cm. The episodes were more frequent for smaller, denser pans, varying from 75 per hour to 24 per hour. The submergence time was typically 10 seconds thus the fraction of the time that these episodes applied is quite small, i.e. 7 to 20% but at higher wind speeds the frequency increases, especially for the smaller pans.

It appears that the pans are subject to a frequency of deep submergence events with a spectrum of eddy sizes and velocities, with smaller eddies being more frequent. An interpretation of the data is that the frequency (per hour) of these events at a wind speed of 5 m/s is approximately

$$N = 500/L$$

where L is the equivalent diameter (cm) in the horizontal plane and the constant 500 depends on wind speed and breaking wave frequency.

The plastic balls, which it was hoped would simulate oil drops, were observed to reside at or near the water surface then occasionally plunge into the water column as a result of a breaking or spilling wave. When there was no wind the low density ($SG = 0.92$) balls rode with the waves and showed little tendency to submerge. As the ball density increased the balls tended to become more frequently and deeply submerged. It was impossible to record the behaviour accurately in the top 5 cm of the water column because of the fluctuating water level. As the water level rose and fell as waves passed the balls rose and fell, but occasionally rising out of the surface and occasionally plunging below the surface. Only a maximum depth could be determined above which the balls spent perhaps 90% of the time. It was also observed that if the pan or ball surface was dry it resisted the spreading of water over its surface and it tended to remain at the surface.

An attempt was made to consolidate the submergence information in an overall mathematical or statistical description. It is believed that one approach is to derive a probability function in which cumulative frequency is plotted against submergence depth for a given oil-ocean system. This would permit statements to be made of the type

"An oil pan of density A and size B , when floating on a water surface at a wind speed C and wave height D will generally spend 65% of the time essentially at the surface, i.e. submerged from a depth of 0 to 2 cm; 20% of the time submerged in the range 2 to 3 cm; 10% in the range 3 to 4 cm and the remaining 5% will be spent at depths below 10 cm. As a result, for a given slick it is expected that 65% of the oil will be essentially at the surface and 35% submerged."

An attractive approach would be to fit a probability density function to the data to express this mathematically, for example, the above data could be expressed by a Weibull type of function of the form

$$P = \exp(-(d/D)^x)$$

where P is the probability that the pan is below the depth d cm, and D is a constant corresponding to the depth of 37% submergence (since when d equals D, P equals 0.37) and x is a second constant reflecting the steepness of the probability curve. For example if D was 2 cm and x was 1.5 the following statistical submergence condition would apply.

Depth d	P	Difference in P
0	1.0	0
1	0.70	0.300
2	0.37	0.330
3	0.16	0.210
4	0.06	0.100
5	0.02	0.040
6	0.005	0.015
<u>>6</u>		<u>0.005</u>
Total		1.000

The pan would be at a depth from 0 to 1 cm for 30% of the time, 1 to 2 cm - 33%, 2 to 3 cm - 21%, etc. until it would only be at a depth exceeding 6 cm, 0.5% of the time.

In practice it was found that, as expected, large low density pans spend almost all their time close to the surface. As pan size is reduced and density increases, the pans are occasionally subjected to episodes of submergence in which under the action of, for example, a breaking wave, they plunge to a depth of perhaps 20 cm then drift slowly back to the surface at a "Stokes Law" velocity.

A tentative correlation is that the constant D is given by an expression of the type

$$D \approx KU^2/(\Delta\rho)^{0.8} \cdot (L + L_0)$$

where K is a constant, U the wind speed, $\Delta\rho$ the density difference, L the pan size and L_0 a constant corresponding to a pan size at which submergence becomes less likely.

It is clear that the submergence phenomenon is complex and difficult to measure and characterize. Further it is likely that the artificial conditions maintained in the wind-wave tank bear little resemblance to those at sea. Thus the primary contribution of this work is not to enable predictions to be made under oceanic conditions, rather it is to enable experiments to be designed in which an assessment can be made of behaviour at sea. Tentatively, we believe that it will be valuable to prepare lard pans of various densities, and sizes, deploy them from a vessel at sea and observe their behaviour, for example how many can be seen at any given time from an elevated platform.

It may also be useful to test the performance of remote sensing systems using lard pans containing an outer layer of weathered crude oil, possibly contained in a plastic bag. It is suspected that sensing systems based on thermal responses may be ineffective because of the overwashing.

Finally, it may be possible to use the submergence data to better predict rates of oil evaporation and dissolution. Submergence will obviously retard evaporation and enhance dissolution, thus most existing models of simultaneous evaporation and dissolution from surface slicks may be quite inappropriate under conditions in which the oil is susceptible to blob or pan formation and submergence.

CONCLUSIONS

The chemical dispersion results tend to confirm the view that the dispersion process occurs in two regimes. The dynamics of the dispersant-oil mixing processes are clearly important determinants of dispersant effectiveness. The preferred strategy is to continue the study of the fundamental mechanism of the dispersion process photographically and by carefully designed experiments in which droplets of dispersant of known size (and preferably in the 200 to 500 μm range) are administered to oil slicks of known properties and thickness and the performance measured.

The submergence study has elucidated to some extent the nature of process by which an oil slick becomes transformed into pans. It is apparent that when an oil slick breaks up into relatively stable blobs or pans, these oil masses become appreciably submerged and will not be easily visible from the water surface. Their thermal (remote sensing) response may not be appreciably different from that of water due to their intimate thermal contact with overwashing water. It is clear that the conventional view that an oil slick remains at the surface until dispersed is erroneous in many cases.

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EFFECTS OF OIL AND CLEAN-UP METHODS ON SHORELINE VEGETATION

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INTRODUCTION

Two experimental oil spills were carried out in the supralittoral zone, both on the same shore. The test area was located on the Atlantic coast of Norway at the outlet of the Trondheimsfjord. Experiment I also included studies of the effects of three clean-up methods. The test oil was the same in both experiments, however the amount of oil and season were different.

EXPERIMENT I

Methods

The experimental spill was carried out in October - November 1983 after the growing season, but before the first snow fell. 10 l m^{-2} oil-emulsion was applied to four $5 \times 5 \text{ m}$ test fields in the supralittoral zone. The vegetation mat was closed with the upper zone being dominated by Filipendula ulmaria and the lower one by Juncus gerardi.

The test oil was a weathered Statfjord crude, which was emulsified (1:1) with seawater.

The test areas (fields I, II, III and IV) were treated as shown in Fig. 1. Sorbent (pine bark) was used as the aftertreatment in all test fields.

Each $0.5 \times 0.5 \text{ m}$ plot was examined with a frame divided into 25 $10 \times 10 \text{ cm}$ small quadrats. The species present were noted in each small quadrat. The permanent test plots were investigated in mid August in both 1983 and 1984.

The degree of cover was subjectively evaluated in each $10 \times 10 \text{ cm}$ small quadrat and the cover in the $0.5 \times 0.5 \text{ m}$ plot calculated from the values of the cover in the small quadrats.

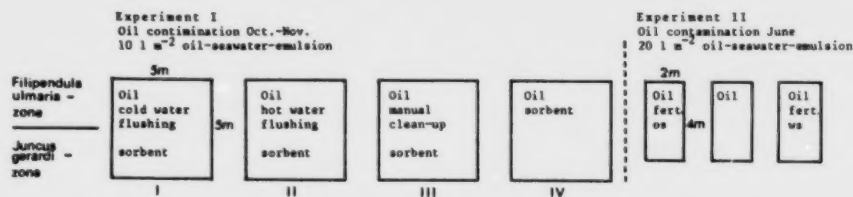


Fig. 1. Design of test fields, experiment I and II

Results

Quantitative effects.

The negative effects on the vegetation cover were small. The reduction in the degree of cover was less than 5 per cent in fields I, II and III. However the negative effect was considerable in field IV. In the upper part of field IV the vegetation cover was reduced by approximately 30 per cent. As the damage was spotwise, it was considered to be an effect of the oil.

In August 1984 (one year after the contamination) the ground was still covered by considerable amounts of oil. Measurements of oil content showed that at the start of the growing season in 1984 the upper parts of fields I, II and III were also covered by some oil. These amounts of oil had not however caused any quantitative damage to the vegetation. If there was any damage caused by the clean-up method it presumably should be most distinct in the upper parts where herbs are dominant since grasses and sedges are generally more resistant to different kinds of mechanical activity. The differences in the values of the degree of cover of the upper and lower parts of fields I, II and III are not significant.

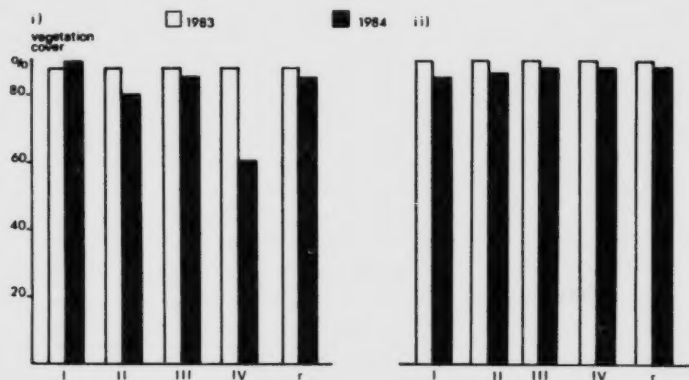


Fig. 2. Experiment I. Vegetation cover.

i) upper parts of test fields ii) lower parts of test fields

Effects on the species level.

Even in a climax community the plant population is not static. The number of individuals varies from year to year, and even if the number of individuals is relatively constant, the turn-over may be extensive (Harper 1976, Baadsvik 1981). It is therefore difficult to know when the effects are small, whether a change in the population size is due to normal population variations or is related to damage caused by oil or the clean-up method.

The number of species was constant in fields I and II but reduced by approximately 25 per cent in fields III and IV. The species which were present in 1983, but were not observed in 1984 are mainly low frequency species except for Armeria maritima which was frequent in fields III and IV in 1983, but was not found alive in 1984. Low frequency species in field III which were present in -83 but absent in -84 were Arrhenatherum elatius, Ranunculus acris, Rhinanthus minor and Taraxacum sp. In field IV, the said species were: Luzula multiflora, Lychnis flos-cuculi and Poa sp.

Field I. Armeria maritima has suffered a distinct reduction in frequency. It is not considered to be very sensitive to an oil spill (Ranwell 1968, Baker 1979). Though A. maritima grows in the lower parts where the oil content is lowest, its reduction is assumed to be an effect of the oil.

Observations in this and other fields show brown and dead rosettes of the species. Damage from a clean-up action could hardly explain such a specific effect. A. maritima is a hemicryptophyt with overwintering organs and buds in the surface of the soil.

It should be assumed that hemicryptophytes are sensitive to an oil spill which occurs during the rest period of plants, particularly those with a sparsely developed root system. A. maritima has however a robust stock-root which is generally considered to be an oil tolerant quality (Baker 1979). Deneke et al. (1975) however report examples of species with stock-roots which are sensitive to oil as they are incapable of escaping an oil contaminated layer by ramification in the manner species with a plural ramified root system can.

Field II. A. maritima was only recorded here in one small quadrat. This rosette was also brown and dead in August -84. Euphrasia sp. and Rhinanthus minor had reduced frequency in -84. Both are annuals with a weak, shallow root system. If the possibility for seed germination is reduced, there is an immediate decrease in the population. This reduction is therefore considered to be an oil effect. The reduction in seed germination frequency by oil is reported by many authors (Plice 1948, Mc Cown & Deneke 1973). A quantitative reduction in the number of annuals is reported elsewhere after oil spill accidents (Burk 1977, Baker 1979, 1983).

Field III. R. minor, Ranunculus acris and Taraxacum sp. had low frequency in -83 and were absent in -84. R. minor is an annual and its reduction is considered to be caused by oil. A. maritima was frequent in -83, but in -84 all the rosettes were dead. Another hemicryptophyt, Leontodon autumnalis suffered a markedly reduced frequency. It is likely that this is also an effect of the oil.

Field IV. The oil content was high in the upper part of the field the following growing season. The upper part was recontaminated with oil from the lower part of the field. L. autumnalis was growing in all 10 x 10 cm small quadrats in test plot 1, but was only recorded in two small quadrats in -84. This species is perennial and the change could hardly be due to a natural population variation. This reduction is likely to be an effect of the oil. Valeriana sambucifolia was growing in the upper part of the field and had increased frequency in -84. V. sambucifolia was propagating by creeping sideshoots from the stem and was therefore able to rapidly colonize an area where the competition was low.

EXPERIMENT II

Methods

The same test oil was used as in experiment I. Three testfields of 2 x 4 m were contaminated with 20 l m⁻² of the oil-seawater-emulsion in June -83. Fertilizer was added to two of the test fields. Two types were used: a commercial N-P fertilizer and an oil-soluble one. The oil-soluble fertilizer was used in the ratio of 1:10, (fertilizer to oil), the water-soluble fertilizer in the ratio of 1:22 to give a comparable C/N ratio. The fertilizers were added immediately after contamination by the oil.

Results

All the above ground vegetation seemed to be killed immediately after the oil contamination. The temperature was relatively high and the emulsion had a low viscosity. This allowed the oil to penetrate into the soil. Measures of oil content in the soil showed relatively constant values the following year (Halme et al. 1985).

The recolonization was slow the first season after contamination, the vegetation cover being no more than 10 per cent in any of the three test fields. There was no quantitative difference between the fertilized fields and the reference. The second year after contamination the growth in the fertilized fields was distinctly better than in the reference, with a 60-70 per cent degree of cover compared to 30-40 per cent in the reference.

The number of species decreased in all the test fields in the first year after contamination. However, the number of species was higher than the reference the second year in all the three oiled fields. There was no difference between the two fertilized fields and the field without fertilizer with respect to the number of species.

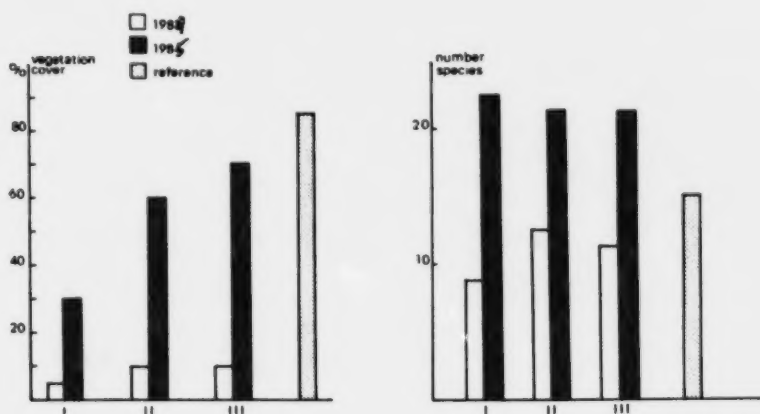


Fig. 3. Experiment II. Vegetation cover and number of species in the test fields.

I - oil and oil-soluble fertilizer, II - oil, III - oil and water-soluble fertilizer. Oil contamination 20 l m⁻² in all fields.

Discussion

Oil can cause damage to plants in different ways; by a direct toxic effect, by changing the soil properties, by "smothering" (preventing gas exchanging) or by changing the competitive relations between species (Baker 1983).

Only a small number of experimental spills on shorelines have included studies of the effect of clean-up methods. Our experiment has not documented any damage to the vegetation as a result of the methods used in this case. This corresponds to the results from similar experiments (Baker 1971 a, b, Mattsson et al. 1981, Bromann et al. 1983). Hot water flushing has however caused a degree of immediate damage (Broman et al. 1983), but the biotop was restarted the next season. On a rocky shore high pressure, hot water flushing had a disastrous effect on lichens and small algae. Mattsson et al. (1981) report that the effect of hot water flushing is as negative as the effect of oil by itself.

A feature of the effect studies which are concerned with the clean-up methods is that they are not followed up over a number of years. There is therefore no documentation about the gains from shortening the time for restoration through a clean-up action.

The only distinct quantitative reduction in vegetation growth caused by oil was in field IV. Similar amounts of oil have often caused more damage to plant life (Mc Cown et al. 1973, Wein et Bliss 1973, Kinako 1981, Mattsson et al. 1981). There are several reasons for this. First, there are different kinds of crude used in the experiments referred to. Our experiment was conducted with a viscously weathered crude in emulsion. A second and main reason for the different results is however considered to be the time of the year when our experiment was carried out. The vegetation was contaminated with oil after the end of the growing season in a rest period for plant life, i.e. a period when the living parts of the plant are well protected. A reduction in damage by contamination in other periods of the year outside of the growing season has also been reported earlier (Baker 1971, Wein and Bliss 1973).

Fertilizers seem to have a significantly positive effect on regrowth after an oil spill, here expressed as the degree of cover. However fertilizers do not seem to have a positive effect on the number of species.

The recolonization after an oil spill seems to follow a normal development for secondary successions which take place after some kind of extensive damage to the vegetation cover. The higher number of species than the reference the second year after contamination indicates a temporary phase before consolidation.

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DEGRADATION RATES OF CRUDE OIL AND PETROLEUM PRODUCTS IN AN EXPERIMENTAL MARINE SAND COLUMN UNDER DIFFERING TEMPERATURE CONDITIONS

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INTRODUCTION

Intertidally stranded oil or oil products are known to contaminate coastal sediments, and depending on the wave energy, bacterial populations, presence of other organic matter, and other factors such as flushing and intertidal pumping, to remain for rather long times. For example, silt and pebble environments such as are found along the Canadian east coast that were oiled by the ARROW spill in 1970 remain contaminated at this time (Vandermeulen, pers. observations).

Far less is known of the fate of oil in sandy sediments. It is known that oil slicks, entrapped as oil layers during normal beach rebuilding as occurs in the early spring of the year, can persist for several years before they are eventually eroded during subsequent beach erosions (Long et al., 1981). However, degradation rates of oil contaminating such sand columns are only poorly understood. Estimates that have been made have usually been based on mineralization of certain specific radioisotopic marker compounds such as the hydrocarbons hexadecane and naphthalene (e.g. Atlas and Bronner, 1981). Less is known of the disappearance pattern of whole oils under these conditions, in sandy sediments by natural weathering processes of physical and microbial degradation.

This study addresses the latter, and specifically examines the influence of temperature on long-term degradation of some oils in sandy sediments that were flushed by seawater containing naturally occurring microbial populations. Aliquots of three different oils - a crude oil, a bunker oil, and a condensate - were buried in an experimental sand column, and incubated at three different temperatures (5, 10, 15 °C). Also, both the presence and the potential to enhance natural degradation were investigated by supplying extra nutrients.

Results indicate that natural degradation rates under these experimental conditions of oil in a sand column were low, even at the highest temperature (15 °C) over several months. At the lowest temperature tested (5 °C), degradation was very low to negligible. However, parallel measurements of degradation of oil in in vitro preparations in shaking flask experiments demonstrated both the presence of hydrocarbon utilizers, and the potential for their enhancement.

MATERIALS AND METHODS

Experimental design

The test chamber consisted of a container fitted with a central standpipe, and placed inside a larger container partially filled with freshly collected natural seawater. The central or test container was filled with 20L of sediment. The outer container served as both temperature cooling bath and seawater reservoir. Water was then circulated between the outer reservoir and the inner test container by means of an airlift pump.

In actual operation, water from the outer reservoir was first passed through a charcoal filter before flowing slowly down through the central standpipe to the bottom of the test container. A perforated ring at the base of the standpipe assured even distribution and flow of seawater to the bottom of the sand column. Return flow was by simple percolation upwards through the sand column to the top where the seawater was allowed to overflow back into the outer reservoir.

In addition to being circulated in this way, a portion of the seawater in the system was exchanged daily with fresh seawater. Although the airlift pump-driven recirculating system could not be controlled very accurately, water flow was steady and continuous, and aerobic conditions were maintained throughout the sediment column.

Table 1. Duration of degradation experiments for each temperature regime with each test oil.

Oil Type	Length of time in the system (months)		
	5 °C	10 °C	15 °C
crude oil	5	6	5
Bunker C fuel oil	5	6	5
Scotian Shelf condensate	4	4	4

The sediment used came from two sources, a commercial silica sand and a beach sand taken from a sandy beach on the eastern shore of Nova Scotia.

Oil exposures

Aliquots of test oil were mixed with known volumes (ca. 25 ml) of sandy beach sediment to a final ratio of about 1:100 by weight, and placed into small bags of fine fiberglass screening. For any one degradation test, twelve duplicates were then buried in the sediment-filled test container.

Long-term degradation tests were run continuously over a period of several months, and oiled samples were taken periodically over the time period for analysis. Experimental time periods are shown in Table 1.

Analyses

During a typical long-term experimental run, ca. 3-6 months, sample bags were removed from the test container at periodic intervals. Analyses carried out on these included total aerobic bacterial counts, and qualitative hydrocarbon analysis using gas chromatography. Parallel bacterial counts were also done on the surrounding sediment column. Throughout, a parallel non-oiled sediment column served for reference measurements.

For hydrocarbon analyses, several methods of sample work-up were investigated. The procedure yielding the best recovery of oil with the highest precision consisted of extraction of the wet sand/oil mixture in dichloromethane using a Soxhlet apparatus, drying with sodium sulfate, and concentrating the extract to ca. 10 ml by rotary evaporation. In this way, recovery of hydrocarbons with boiling points $\leq$ C13 was about 93%, with a precision on peak areas between analyses of $\pm$ 5%. Analysis was by capillary GC (silicone fused-silica column).

Quantitative estimates of degradation of oil in the experimental setup were obtained by determining a number of indices from chromatograms. For crude oil and Bunker C these included ratios of C17:pristane, C18:phytane, C18:unresolved maximum and C21:unresolved maximum, all referenced to fresh crude oil. For condensate four different hydrocarbon ranges were compared.

Enhancement experiment

Hydrocarbon degradation measurements were done in vitro under a variety of conditions using a series of shaking flasks kept in a constant temperature environment. The conditions included two types of sandy sediment (commercial silica sand, beach sand), two oil concentrations (1% and 10% by weight), naturally available and enriched nutrients (0.66 g K₂HPO₄, 0.41 g KH₂PO₄, 0.1 g MgCl₂·6H₂O, 0.05 g FeCl₂·4H₂O, 0.002 g MnCl₂·4H₂O, 1.0 g (NH₄)₂SO₄ per L water) (Environment Canada 1978) using both naturally present and enriched microbial populations. For the latter, inocula of hydrocarbon degrading populations obtained from a culture grown on the test crude oil were added to the flasks. Results were expressed as total plate counts.

RESULTS

Long-term degradation experiments

Results of the chromatographic analyses from the long-term experiments with the three test oils are shown in Tables 2, 3 and 4.

In the crude oil experiments, some loss of hydrocarbon material was evident at 10 °C and 15 °C after 4 and 2 months respectively. Part of this loss was due to simple leaching out of hydrocarbons due to flushing

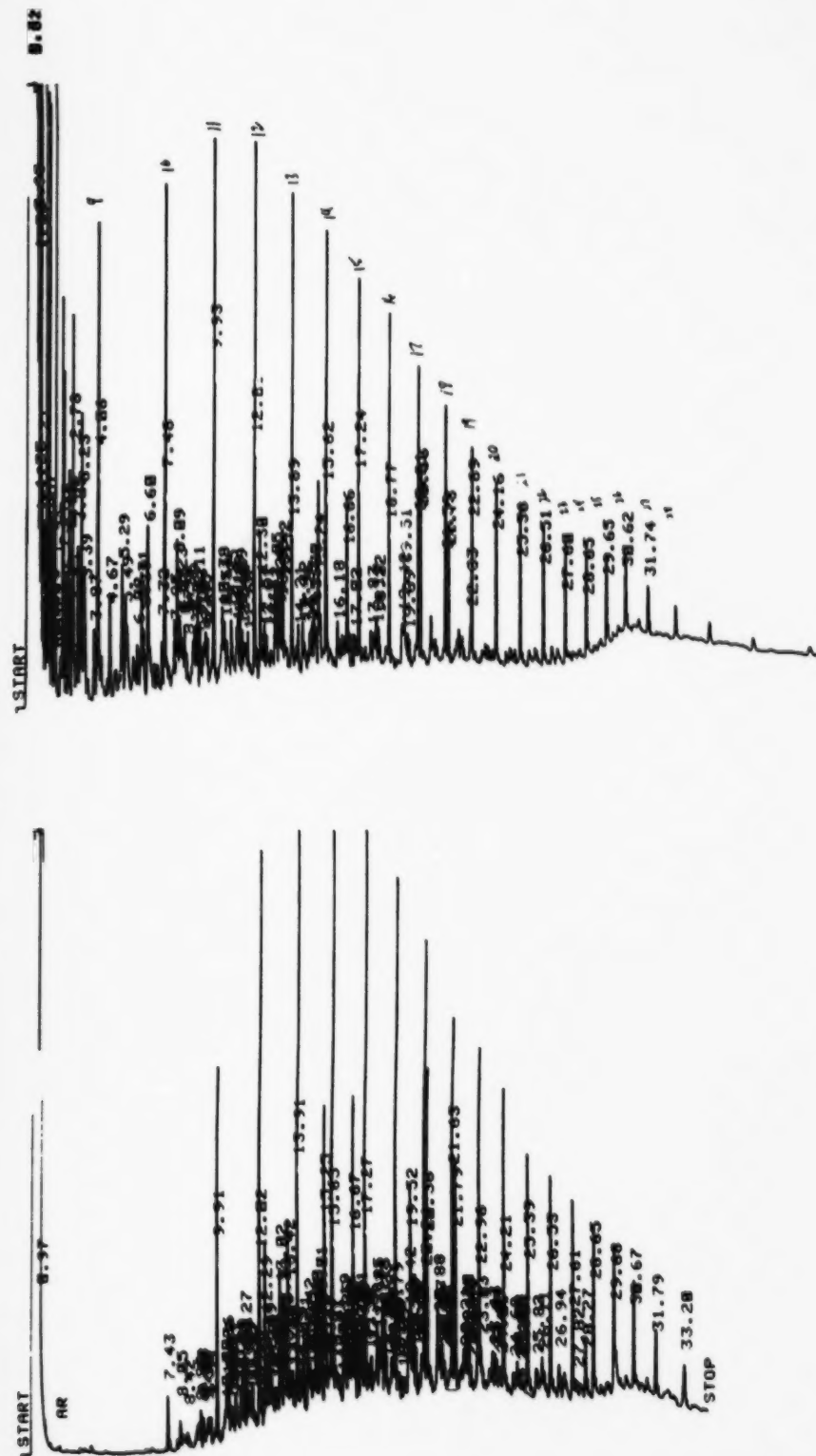


Figure 1. Gas chromatograms of crude oil standard (upper) and after 11 weeks degradation in sand column at 10°C.

Table 2. Changes in marker indices in GC-chromatograms from crude oil exposed in experimental sand column in long-term exposure study.

Temperature	time (months)	% below C10	C17: pristane	C18: phytane	change in UCM*
reference oil	-	25	1.30	1.45	-
5 °C	1 mo	3.77	1.23	1.43	negligible
10 °C	1 mo	1.0	1.26	1.42	negligible
10	3 mo	1.0	1.14	1.26	< 5%
10	4 mo	8.0	1.27	1.37	< 10%
15 °C	2 mo	1.7	1.23	1.37	< 10%

* unresolved complex mixture.

Table 3. Changes in marker indices in GC-chromatograms from Bunker C fuel oil exposed in experimental sand column in long-term exposure study.

Temperature	time (months)	% below C11	C17: pristane	C18: phytane	change in UCM
Bunker C reference oil	-	0.5	1.58	1.55	-
5 °C	1 mo	0.3	1.42	1.55	negligible
5	3 mo	<0.1	1.37	1.55	negligible
10 °C	1 mo	<0.1	1.50	1.60	< 5%
10	2 mo	<0.1	1.43	1.55	< 5%
10	3 mo	<0.1	1.44	1.52	5%
15 °C	1 mo	<0.1	1.42	1.49	< 5%
15	2 mo	<0.1	1.41	1.47	<10%
15	3 mo	<0.2	1.56	1.50	10%

Table 4. Changes in marker indices in GC-chromatograms from condensate exposed in experimental sand column in long-term exposure study.

Temperature	exposure time	% eluted in n-hydrocarbon range			
		C6-C10	C10-C14	C14-C17	C17-C26
reference oil	-	48.5	27.6	19.1	4.8
10 °C	3 months	24.8	44.8	26.2	4.2
15 °C	3 days	44.0	n.d.*	n.d.	n.d.
15 °C	6 days	43.0	n.d.	n.d.	n.d.
15 °C	3 weeks	40.0	n.d.	n.d.	n.d.
15 °C	2 months	35.9	37.9	21.6	4.6

n.d. = not determined

Table 5. Microbial data (total plate counts) after 3-week nutrient enhanced crude oil exposure in sandy sediments. Cultures contained either natural environmental microbial populations, or had received an additional inoculum (10 mL⁻¹) of a laboratory-grown enriched population. Numbers in brackets () refer to sample numbers as in Table 6.

Crude oil %	crude	crude silica	crude beach sand	crude/sterile beach sand	crude beach sand nutrients*
<u>natural microbial population</u>					
1% crude	(1)* 8.0×10^5 2.0×10^4 F	(2) 2.3×10^6 1.3×10^6 F	(3) 1.4×10^9	(4) 2.0×10^9	(5) 1.2×10^7
10% crude	(6) 9.0×10^4 2.3×10^4 F	(7) 2.3×10^5 1.6×10^6 F	(8) 8.0×10^8	(9) 1.1×10^9	(10) 3.3×10^7
<u>inoculated</u>					
1% crude	(12) 1.2×10^7 1.5×10^9 F	(12) 4.9×10^6	(13) 1.4×10^9	(14) 2.3×10^9	(15) 1.5×10^8
10% crude	(16) 6.5×10^4	(17) 2.2×10^7	(18) 2.1×10^8	(19) 1.1×10^9	(20) 3.0×10^8

F=fungal counts

Table 6. Crude oil degradation indices after 3-weeks nutrient enhancement. Values given are ratios of peak areas from chromatograms. Sample numbers are the same as those listed in Table 5.

	Sample no.	Treatment	C17: pristane	C18: phytane	C18: UCM	C20: UCM
fresh crude			1.43	1.33	3.8	3.0
natural						
1% crude	1	oil alone	0.59	0.37	0.69	0.33
	2	+ silica	1.47	1.01	2.2	1.3
	3	+ beach sand	0.83	0.43	0.30	0.18
	4	+ sterile "	0.20	0.17	0.34	0.12
	5	+ nutrients				
		+ beach sand	0.23	0.10	0.12	0.10
inoculated						
1% crude	11		0.91	0.53	1.3	0.58
	12	+ silica	0.12	0.10	0.17	0.11
	13	+ beach sand	0.59	0.42	0.34	0.13
	14	+ sterile "	0.20	0.21	0.30	0.11
	15	+ nutrients				
		+ beach sand	0.77	0.23	0.13	0.10
10% crude						
	16		1.0	0.48	0.74	0.60

away with the water circulation. This was observed in all cases, even after only a few days of operation.

In addition, there were some compositional changes that could be ascribed to selective degradation (see Figure 1). This was generally less than 10% of the original reference material.

In the Bunker C experiments, the same parameters were monitored as for the crude oil experiments, except that C11 was used instead of C10. The latter was frequently lost from the chromatograms. Again, some loss of peaks was observed that could be ascribed to degradation (Figure 2). Less change was noted in the C17:pristane and C18:phytane ratios with Bunker C than with crude oil. However, the change in UCM for Bunker C was greater than was observed with the crude oil experiments.

There was little evidence of degradative changes in the condensate, even after 3 months at 10 °C and 4 months at 15 °C (Figure 2). However, a significant fraction of the lower molecular weight materials appear to have been lost, probably by leaching - up to 50% loss at 10 °C, and up to 26% loss at 15 °C.

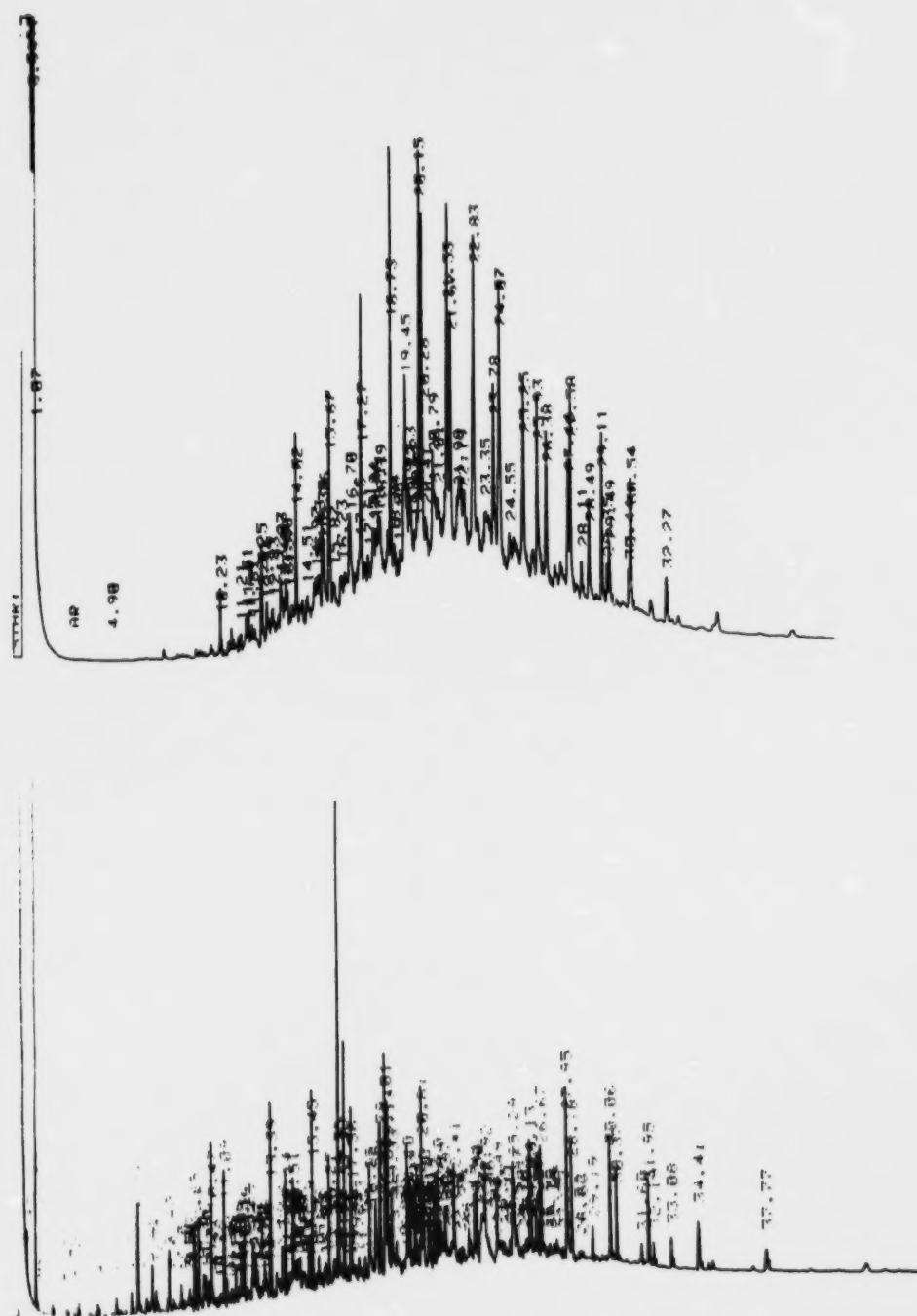


Figure 2. Gas chromatograms of Bunker C fuel oil (upper figure) and condensate (lower figure) after 3 and 4 months in the experimental sand column at 15 °C.

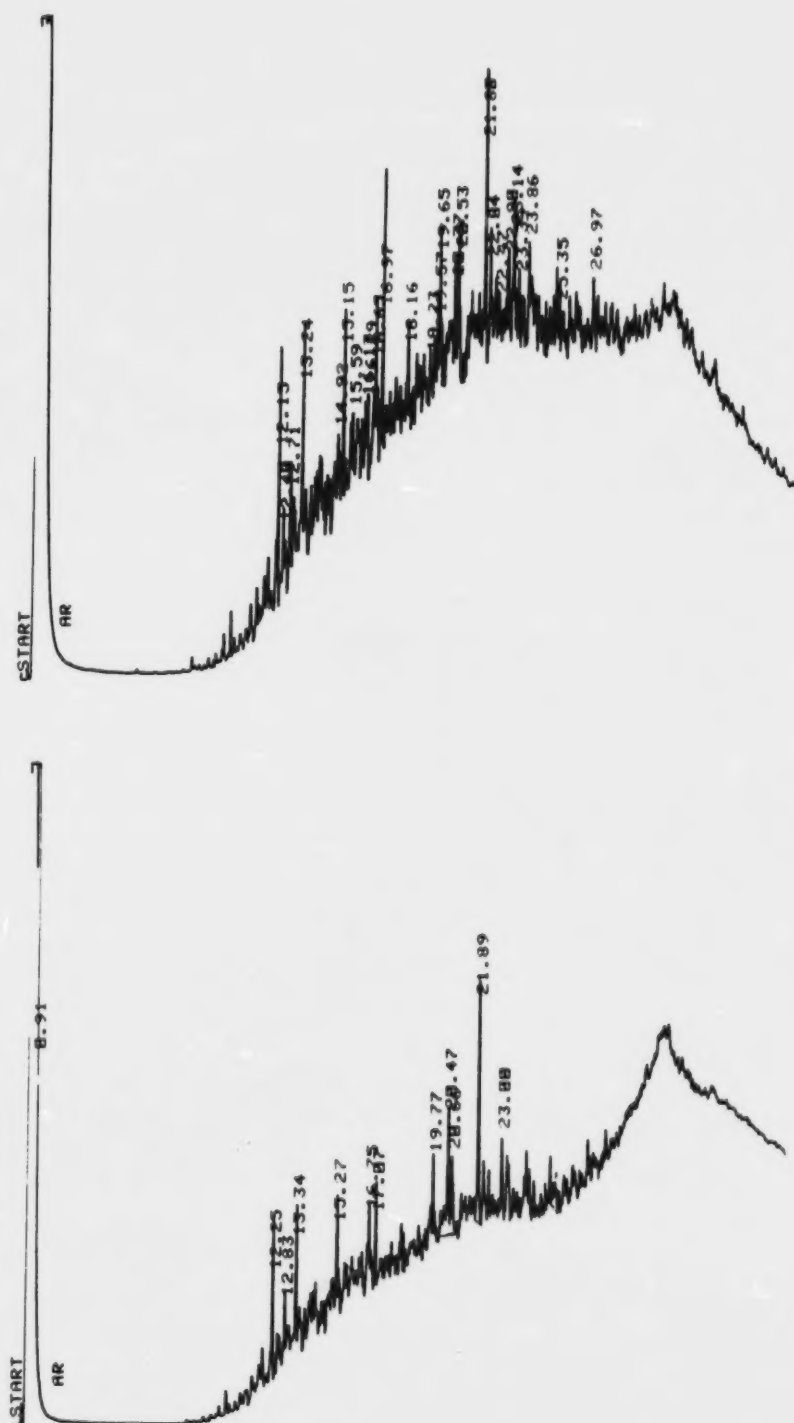


Figure 3. Gas chromatograms of crude oil from nutrient enhancement experiments. 10% crude oil in beach sand with nutrients (upper), and 1% crude with same conditions (lower). Numbers 10 and 5 respectively in Table 5.

Enhancement study

Bacterial/fungal data from the shake-flask incubation experiments are listed in Table 5, and concomittant hydrocarbon degradation data in Table 6.

Generally, the plate series containing beach sediment had higher numbers of bacterial colonies than those without (Table 5). This probably explains the absence of fungal growth on those plates as a result of bacterial crowding. Total plate counts, after 3-weeks incubation, did not differ greatly for the various treatments. Lowest counts were obtained in flasks containing crude oil only, while consistently highest values were obtained in flasks containing a combination of crude oil and beach sand. Nutrient-enhanced preparations were an order of magnitude lower, after the three week incubation.

For comparison, total plate counts for samples taken from an experimental sand column were similar initially to those obtained with crude oil alone - 6.8×10^4 (July 2), 1.0×10^4 (July 7), 7.9×10^4 (July 24) - but increased with time - 1.1×10^6 (September 3).

While the microbial data did not vary greatly, the hydrocarbon degradation patterns did differ markedly from freshly analyzed oil reference material (Table 6). In all cases the ratios changed significantly, with marked losses in the aliphatic components (reflected by the decreasing ratios of C17 and C18 to pristane and phytane respectively), and increases in the unresolved material under the UCM envelope (see Figure 2).

DISCUSSION

The results from the long-term (3-5 months) degradation experiment with the experimental sand column indicate that under those conditions, with the primary input of microbes from the circulating seawater, degradation proceeds very slowly. Decreasing the temperature of the incubation further reduced the degradation process, to where it proceeded at a very slow or negligible rate.

We suspect that in fact these results very reasonably duplicate process rates that can be expected in the field, suggesting that, under real environmental conditions, the degradation of oil stranded within sandy north-temperate beaches will probably proceed very slowly.

The shaking-flask nutrient-enhancement data, however, suggest that while degradation may be a slow process under simulated environmental conditions, the potential for much higher degradation does exist. Indeed, in several of the experimental flasks there were essentially no normal hydrocarbons remaining, except for a large amount of unresolved material found under the unresolved complex envelope.

From an environmental point of view, the latter conditions might be found in the field in tide pools and other exposed intertidal situations, rich in organic matter.

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FISH TAINTING AND HYDROCARBONS IN THE ENVIRONMENT: A PERSPECTIVE

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1. INTRODUCTION

Under the Effects Monitoring priority study area, the Environmental Studies Revolving Funds initiated a study in 1984 to review the question of possible fish tainting caused by the introduction of hydrocarbons into the marine environment as a result of offshore oil and gas exploration and development activities.

The objectives of the study were:

- To review case histories to attempt to identify concerns associated with tainting and determine how recorded incidents have been handled in other jurisdictions;
- To assess the validity of available assessment techniques and analytical methods for determining whether or not a product is tainted;
- To recommend a series of investigations to develop a reasonable scientific basis for conducting an evaluation of a possible tainting situation.

Essentially, the study was designed to provide an overview of the subject and identify a possible future course of action which the Funds may choose to pursue with respect to tainting. The study concentrated on the scientific aspects of the problem and avoided the perceptual questions (e.g. marketing, economic impacts) for which little factual information is available. This paper contains a summary of the study findings and attempts to place the subject of tainting in some perspective.

2. BACKGROUND

Tainting is the development of an unnatural flavour in finfish and shellfish as a result of exposure to contaminants present in an aqueous medium. Tainting is not caused solely by hydrocarbons but the strongest tainters tend to be organic compounds. It is one human-related effect associated with the bioaccumulation by marine organisms of more soluble, polar as well as cyclic and aromatic hydrocarbons, artificially introduced into the aquatic environment.

Although it is only one element of the hydrocarbon contamination problem, real or potential tainting associated with petrogenic hydrocarbons, i.e. condensate and crude oil, has become a concern to fishermen because of the increasing exploration, production, and transportation of oil at sea in recent years (GESAMP, 1977). Until recently, this concern has not been matched by concerted scientific or regulatory effort at national levels or

within the international community to develop mechanisms for dealing with the problem (GESAMP, 1983). Currently, there are no generally accepted standard scientific methods for assessing or verifying tainted produce (Howgate, pers. comm.).

For the purposes of this study, a basic definition of the term "tainting" developed by the GESAMP Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (EHS) (GESAMP, 1985) is considered as generally applicable for finfish or shellfish prior to processing.

"(Tainting is) the development of a flavour or odour in the organism when caught or harvested which is not typical of the flavour or odour of the organisms themselves."

It should be noted that this definition does not make a statement about the nature of the atypical flavour or odour or attempt to quantify the degree of taint. The importance lies in whether the flavour or odour of the product is altered, not whether a contaminant impairs or improves the flavour.

The EHS Working Group (GESAMP, 1985) have noted that there is one order of magnitude difference in contaminant concentrations between the detection and recognition thresholds of off-flavours. It is important to remember that it is the off taste, not the determination of what is causing the off flavour, which will cause product rejection.

Tainting of seafood produce can arise from either the natural spoilage of improperly handled whole or processed produce, or the exposure of living organisms to anthropogenic contaminants present in the aquatic environment. The latter is of greatest concern because it can result in substantial economic losses to innocent parties (GESAMP, 1977). Economic losses as a result of perceived or actual tainting associated with hydrocarbon losses are impossible to evaluate because of inadequate documentation, and technical data on the subject are sparse (GESAMP, 1982).

Fear of tainting can be as serious a problem as an actual tainting incident. Consumer resistance, closures imposed by regulatory authorities, and embargoes on harvesting activities by producers resulting from even the remote possibility that seafoods are tainted can cause severe economic losses. Tainting per se is essentially an economic problem associated with the wider environmental or public health concerns arising from exposure of exploited fish stocks to anthropogenic hydrocarbons and is as much a perceptual problem as a real concern. Unlike the presence of carcinogens such as PNAH, which are known to bioaccumulate but are not detectable by normally human sensory systems, the presence of hydrocarbons causing a taint is readily detectable.

Tainting is a difficult subject to treat quantitatively because it is a sensory perception based on individual experience and preference. The flavour of a food is determined by a blend of taste and odour evoked by a substance in or near the mouth. As a sensory perception, individual experience as well as preference can greatly influence a determination as to whether a product is "off". In fish, the flavour can be strongly influenced by the diet of the living organism prior to harvesting, as well as by natural degradation or spoilage after death. Separating flavours associated with natural processes, compared with those resulting from exposure to contaminants such as hydrocarbons released into the environment, can be difficult.

From the point of view of marketability of fish and shellfish and accep-

tance or rejection of a product by inspectors and the public, not only raw odour, but also tissue or shell colour, tissue texture, and general aesthetic quality of the product will influence the decision. External contamination or fouling by hydrocarbons, as well as a taint, may be cause for product rejection, although external contamination of an organism does not necessarily mean that tainting of the underlying tissue has occurred (GESAMP, 1977). Generally, tainted product can be readily detected by initial grading but in rare cases, the potential presence of an "off-flavour" or taint may not be detectable until the product is prepared for eating or is actually consumed.

Increases in body burdens of hydrocarbons leading to the acquisition of a taint arises from four mechanisms (Connell and Miller, 1981). These are:

- Absorption of hydrocarbons on the skin;
- Absorption of dissolved hydrocarbons from the water through the skin;
- Absorption of dissolved hydrocarbons through the gills, i.e. respiration; and
- Ingestion of food contaminated with petroleum.

The mechanism varies from situation to situation depending upon the species exposed, the type and concentration of hydrocarbons present, the exposure time, and the season. Generally, the increase in body burden is reversible but the depuration rate varies. This is important because it means that live contaminated produce which has acquired a taint need not be destroyed. Placement of produce in uncontaminated holding facilities for a period of time will restore product quality and should not compromise market acceptability.

Tainting as a result of absorption on the skin has been observed when a catch has accidentally come in contact with oily water from storage tanks (Stansby, 1978) or from fouled nets. The contaminant and to some extent the acquired odour can be removed by washing in running water and detergents although a residual odour may remain after cleaning.

Each species of finfish and shellfish has its own characteristic flavour (McGill *et al.*, 1984). The flavouring components occur in both the lipid and the protein of the fish. Ordinarily, however, in the absence of putrefaction, the most volatile and flavourful components are the chemicals dissolved in the lipid (Stansby, 1978). It is generally accepted that there is a greater storage and persistence of aromatic and polynuclear hydrocarbons in lipid-rich than in lipid-poor tissues of most marine species (GESAMP, 1977). Whittle and Mackie (1976) have suggested that the amount of "free" lipids present in a fish indicates the susceptibility of that organism to acquire a taint.

Although the total lipid content is important with respect to bioaccumulation, the lipid content of edible tissue may only be important with respect to the presence of a taint. Hence, for most groundfish where the lipid content of edible tissues is low (<3% wet weight), the susceptibility to acquiring a taint is far less than for pelagic species such as herring (*Clupea harengus*) and mackerel (*Scomber scombrus*) where the lipid content may be as high as 20-24% of the wet weight of edible tissue. The lipid content of the muscle can show marked seasonal variation which is reflected in the tainting potential, or the threshold concentrations at which an off-flavour is noticeable.

In shellfish, the distribution of taint producing hydrocarbons in organisms varies. In molluscs, they would tend to be widely distributed while in

crustaceans, they would tend to be concentrated in the hepatopancreas which is normally not eaten. Exposure of crustaceans may not necessarily lead to tainting, but releases of metabolized hydrocarbons from the hepatopancreas may lead to relatively long term low level contamination in the edible tissue. This may or may not impair the taste.

The threshold level of exposure necessary to cause a taint in finfish and shellfish depends on the chemical composition of the hydrocarbon contaminant and on the species affected. Tainting has been associated with diesel fuel (Mackie et al., 1978), crude oil (Motohiro and Inoue, 1973), Bunker C (Shenton, 1973; Scarratt, 1980), and gasoline (Kerkhoff, 1974) present in the environment, as well as with refinery effluents (Nitta 1972; Connell, 1974). The principal components of crude and refined oil causing tainting include the phenols, dibenzothiophenes, naphthenic acids, mercaptans, tetradecanes and methylated naphthalenes (GESAMP, 1977). Some of these compounds are polar, some volatile, and most are somewhat soluble in water and lipids. Due to their lipid solubility they are readily transferred by partitioning into the blood and tissues of organisms. Due to metabolic processes of organisms that alter the chemical characteristics of contaminants, it is difficult to unequivocally identify, by chemical analytical techniques, compounds in crude oil or condensates that exactly match hydrocarbons isolated from fish deemed to be tainted. The chemical verification of tainting is also difficult due to biogenic hydrocarbons produced by the living organisms themselves. Pristane, some n-alkanes and isoprenoid hydrocarbons are widespread in the food chain (GESAMP, 1977) and overlap to a large extent with petrogenic hydrocarbons.

Given this rather complicated background, it is not surprising that there is considerable contradiction in the literature on the subject of tainting. As indicated above, it is a subject that has received relatively little systematic attention from the scientific community until recently. The study revealed a number of areas where information is lacking or available evidence is conflicting on the subject of tainting. The principal findings of the study are described in the following section.

3. SUMMARY OF FINDINGS AND RECOMMENDATIONS

The discussion which follows is divided into three subsections - case histories, regulatory mechanisms, and methods of determination. In each, the results of the study are summarized and the conclusions drawn are highlighted.

3.1 Case Histories

Available case histories of tainting of marine organisms resulting from oil pollution were reviewed in an attempt to identify the common factors associated with incidents of reported tainting and the responses of regulatory authorities to a real or perceived tainting situation. The case histories were broken down into tainting arising from industrial discharges, shipping accidents, and offshore oil and gas activities. Much of the available information about tainting incidents is anecdotal, or is located in government reports and the gray literature which cannot be readily accessed (GESAMP, 1982).

Tainting incidents and residual tainting is generally associated with

organisms present in shallow protected coastal waters where circulation is limited. It is more often associated with shellfish than finfish. To date, most of the tainting incidents have arisen from shipping accidents involving losses of large volumes of crude oil, or distillate into confined coastal waters. Relatively few instances of tainting have been reported as a result of industrial discharges into marine waters.

Numerous shipping accidents have resulted in reported tainting but the best documented cases are the Torrey Canyon and Amoco Cadiz incidents where incidents of shellfish and finfish contamination were reported (e.g. Shelton, 1982). In the Amoco Cadiz case, considerable economic losses in the oyster industry were experienced (Chassé, 1978). Generally, available information indicates that the fisheries affected by an oil spill resulting in tainting gradually recover, and long term impacts are not apparent. In Canada, tainting as a result of shipping accidents has not been reported but it has been a concern to authorities (see Scarratt, 1980).

The study revealed that little, if any, contamination has occurred as a result of blowouts associated with offshore oil and gas activities. The Ekofisk and Uniacke blowouts did not cause discernable tainting although, in both situations, some evidence of hydrocarbon exposure was apparent (Whittle *et al.*, 1978; Zitko *et al.*, 1984). There were no other discernible effects on the fisheries as a result of these incidents. Tainting was not reported during or after the Ixtoc blowout although there were other impacts on the fisheries. The only recent documented case of seafood becoming tainted was as a result of the Funiwa 5 blowout in the Niger Delta.

The risk of tainting is higher in coastal waters than in offshore areas. Where blowouts at offshore wellsites have occurred and oil or condensate released during the accident has not reached the coast, fish tainting as a result of hydrocarbon uptake from the dissolved or particulate material in the water column has not been apparent. The hydrocarbons are rapidly dispersed in the environment and concentrations rapidly decrease to levels below which exposure of organisms will cause a taint. In coastal areas, the hydrocarbons do not disperse as quickly and can become trapped in sediments. These factors substantially increase the risk of finfish and shellfish resources acquiring a taint as a result of a spill.

Of particular interest from the oil spill countermeasures standpoint is the finding that dispersant usage after a spill in the past has been responsible for fish resources in coastal areas becoming tainted. The risk of this is now thought to be lessened because of the chemical composition of the second generation dispersants, but some doubt remains.

3.2 Regulatory Mechanisms

The regulatory mechanisms within the 19 jurisdictions canvassed during the study revealed that few countries have established protocols for dealing with a tainting incident. Monitoring produce for tainting is usually the responsibility of public health authorities who only act to condemn produce deemed to be unwholesome after landing. Closures are occasionally imposed. They are not a consistent practice and fishermen are responsible for deciding where and when to fish. In some cases, fisheries authorities have the power to invoke closures but firm guidelines for determining when a fishery may be reopened after a tainting incident are lacking.

From the review, it is evident that regulatory responsibility for manage-

ment of a tainting incident is generally fragmented. The exception is in the United Kingdom where the Food and Environment Protection Act specifies the responsibilities of the various authorities in the event of a spill of toxic substances.

Where major spills of hydrocarbons from tanker incidents or offshore well blowouts have occurred, large exclusion zones established to ensure public safety and to facilitate cleanup or well-capping activities have, as a side-effect, led to a temporary fishing closure. These closures are not enforced after the emergency has passed and as indicated above there are no established procedures for determining the quality of affected finfish and shellfish resources before a fishery is reopened.

3.3 Methods of Determination

Determination of suitable methods for identifying a taint proved to be a relatively easy task compared with the subjects considered above. Methods for determining taste quality are well developed in the food sciences, and chemical analytical methods are available. The literature on the latter is voluminous. From the determination of taint standpoint, the real concern is developing suitable and consistent methods for separating natural flavours, and variants thereof, from those introduced as a result of exposure to hydrocarbons.

Because tainting is a sensory perception, sensory (organoleptic) methods are required to evaluate the quality of suspect produce. Sensory testing, however, is subjective and is difficult to quantify. On the other hand, chemical analysis of the product will yield quantitative results, but will only identify the types of hydrocarbons present and will not always identify the taint-producing agent. Chemical analysis will not, by itself, determine whether a product is tainted.

Sensory evaluation methods involve using the senses of taste and odour to establish differences or preference of a suspect product with a known standard or control. Trained or untrained people assembled in a taste panel are used in the comparison. Specific sensory methods include the triangle test, multiple comparison test, a hedonic test, and category scaling. The method chosen depends on the number of samples, quantity of product available, the information desired, and the qualifications of the panel members. In any evaluation to identify a possible taint, the objective is simply to determine whether there is a detectable difference in the taste of produce from contaminated and uncontaminated areas, and not to classify the nature of any difference. Using this premise, it was concluded that the basic triangle test would prove to be the most useful and reliable tool to identify a possible taint. This is consistent with the GESAMP (1985) recommendations.

Sample preparation for these tests is critical. It would appear that the "boil-in-a-bag" method is preferable to the casserole method because it is easier to standardize and results should be more readily reproducible. Variations in oven temperature and sample handling associated with the casserole method could inadvertently bias the results.

The review of chemical analytical techniques determined that the most suitable method involves mincing the sample and subjecting it to steam distillation, followed by hexane extraction of the distillate, drying and concentration. Hydrocarbon determinations should be made using capillary GC-MS. The method is proven and has the advantage of speed and simplicity.

As a procedure to support sensory evaluations, the chemical analysis should concentrate on the same tissues (e.g. fish fillet, whole oyster, scallop muscle, etc.) that have been tested by taste panels.

To date there has only been limited research to establish a relationship between sensory testing and chemical analysis. In the case of hydrocarbon contamination, case histories provide little guidance in this area because the methods used are often only very generally described in available reports. Where comparisons have been made, it has proven difficult to specifically identify the tainting agent because of biomodification and masking by biogenic hydrocarbons.

3.4 Recommendations

Seven recommendations were developed from the study. In summary these were:

- Standardization and refinement of sensory evaluation methodologies to insure reproducible results and to satisfy any legal requirements for handling compensation claims;
- Correlation of taste panel results with tissue analysis to attempt to establish threshold concentrations;
- Establishment of depuration rates for contaminated fish;
- Establishment of background levels of aromatic hydrocarbons in stocks resident near exploration areas;
- Monitoring of possible uptake of hydrocarbons from production water discharges;
- Determination of the effects of dispersant usage during an oil spill on the risk of tainting; and
- Assessment of the risk of tainting from oil present in sediments or in drilling muds.

By design, the recommendations did not extend into the consideration of perceptual problems associated with tainting. It was felt that if the problem of tainting can be placed on a more factual basis, perceptions can be readily dealt with.

It is recognized that the recommendations cover a wide range of scientific subjects associated with the problem of tainting and may in fact duplicate some work already done. However, the widely divergent results published in the literature suggest that some reappraisal work is needed if we are to be in a position to effectively deal with a fish tainting situation should one arise in Canadian waters in the future.

4. FUTURE DIRECTIONS

This final section contains some general observations arising from the study and ideas which perhaps should be considered when planning future work on the subject of fish tainting.

4.1 Scientific

Although the effect of hydrocarbon contaminants on the quality of exposed finfish or shellfish is well known, there are a large number of scientific questions which remain outstanding. Although the EHS Working Group of GESAMP has been evaluating the effects of hazardous substances carried by ships over a period of 12 years, the question of tainting only

formally entered their deliberations in 1981. Recently, the group has devoted considerable effort to developing a reasonable definition of the term tainting, organoleptic testing protocols for determining a taint and attempts to determine the threshold concentration of tainting substances (see GESAMP, 1983, 1985). It is generally recognized that considerable effort is needed to attempt to systematize the process of evaluating a taint, and place it on a more quantifiable basis. The committee has recognized that the primary method of evaluation must be sensory, and that it would not be valid to base measurement solely on chemical analysis. Crude oil is not considered within the mandate of the working group although many of the derivatives (e.g. benzene, cyclohexane, etc.) have been assigned hazard profiles. The deliberations of the group reflect the scientific complexity of the problem and reinforce the recommendations made for further investigation described above.

Some recent work on tainting and threshold concentrations has been undertaken in the United Kingdom (McGill, pers. comm.) and the results will be published in the near future.

At the risk of restating the obvious, it is evident that the most recent work should be reviewed in detail, before any future programs are finalized.

4.2 Economic and Regulatory Aspects

From the point of view of impacts, tainting is probably the most tangible potential effect of a large scale oil pollution incident on the fishing industry, not because of problems of off-flavour but rather because of problems of marketing. It is a scientific problem which also manifests itself as an economic issue. In a situation where produce is harvested from a well-defined area near or adjacent to a spill site, uncontaminated material may have to be withheld from market in order to protect future markets, or present investments. During the Amoco Cadiz incident, the oyster industry in Brittany was forced to destroy in excess of \$2 million worth of produce (Chassé, 1978). Obviously, fishing operations in coastal waters will be more vulnerable to these pressures than harvesting activities offshore. The risk is increasing substantially because aquaculture facilities on the east and west coasts contain stocks of finfish and shellfish which are vulnerable to acquisition of a taint as a result of chronic or acute oil pollution. The investments in these facilities are substantial.

To date, the regulatory focus related to tainting has been the protection of public health. In Canada, as elsewhere, regulatory responsibility for tainting is somewhat fragmented with both the Departments of Fisheries and Health and Welfare having some responsibilities. Fisheries has primary responsibility for monitoring fish quality during landing and processing to ensure that unwholesome product does not reach market, but if a health question is raised in the market place, health officials become involved. The orientation of both groups is, of course, to protect public health but there may be a need to reorient Fisheries inspection practices at the outset of a pollution incident to protect the industry. It will be argued that this would be unjustified intervention, but the present level of public investment in many fishing related enterprises through loans, grants and subsidies, is such that some regulation of the produce entering the market place may be justified to protect this investment.

A conundrum for regulatory agencies is the qualitative methods available for assessing possible taint. We only have to consider the recent "tainted

tuna" affair to realize that the subjective nature of a decision to accept or reject product is vulnerable to outside pressure. The GESAMP EHS Working Group's guidelines for sensory testing for possible taint place existing methods on a more legitimate basis. Their adoption as a standard testing method would remove the element of suspicion about the validity of the test methods.

5. ACKNOWLEDGEMENTS

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SIMULATION OF OIL BIODEGRADATION UNDER AN ICE COVER

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INTRODUCTION

The environmental studies associated to the exploration, the exploitation and the transportation of oil in extreme weather conditions have received an increasing attention from the Canadian and U. S. authorities and also from oil companies in the recent years. Most efforts have been devoted to the development and the application of countermeasure technology for the Arctic spill response (PISTRUZAK, 1981; HILLMAN 1985; SWISS *et al.*, 1985; SMITH and DIAZ, 1985). Research and development projects were settled to solve particular problems caused by the presence of ice in the application of classical countermeasure techniques such as mechanical clean-up, use of chemical dispersants and burning in-place. In order to improve existing countermeasure technology and allow the development of new techniques, basic knowledge about the physical and the chemical behaviors of the system 'OIL, ICE and ADDITIVES' is required. At a microscopic scale, we need to improve our knowledge about the long-term chemical behavior of the oil when incorporated into solid ice (NELSON and ALLEN, 1981), when adsorbed by unconsolidated ice, when transported and dispersed by drifting ice floes, and also when the oil is chemically dispersed under an ice cover in a low energy environment.

As long-term experiments on ice field could be quite expensive and also highly hazardous in an area such as the St. Lawrence Estuary, we decided to develop and set up a low cost simulation apparatus which could be used to study the long-term fate and the chronic toxicity of crude oil in seawater at low temperature and preferably in presence of an ice cover. We report hereafter a full technical description of our simulator prototype and we also present preliminary results of a biodegradation experiment conducted during the 1986 winter and settled to explore the capabilities of the simulator.

MATERIALS AND METHODS

The Figure 1 shows a schematic representation of the simulator prototype as it was built on the Pointe-au-Père harbour neighbouring our wet laboratory in October 1985. Our research facilities are located near Rimouski on the St. Lawrence Estuary south shore about 300 km east from Quebec city. The heart of the simulator is a stainless steel cylinder (i.d. = 1.20 m) with a conical bottom which fits tightly into a larger steel cylinder (i.d. = 1.40 m) leaving about 10 cm between the walls for the

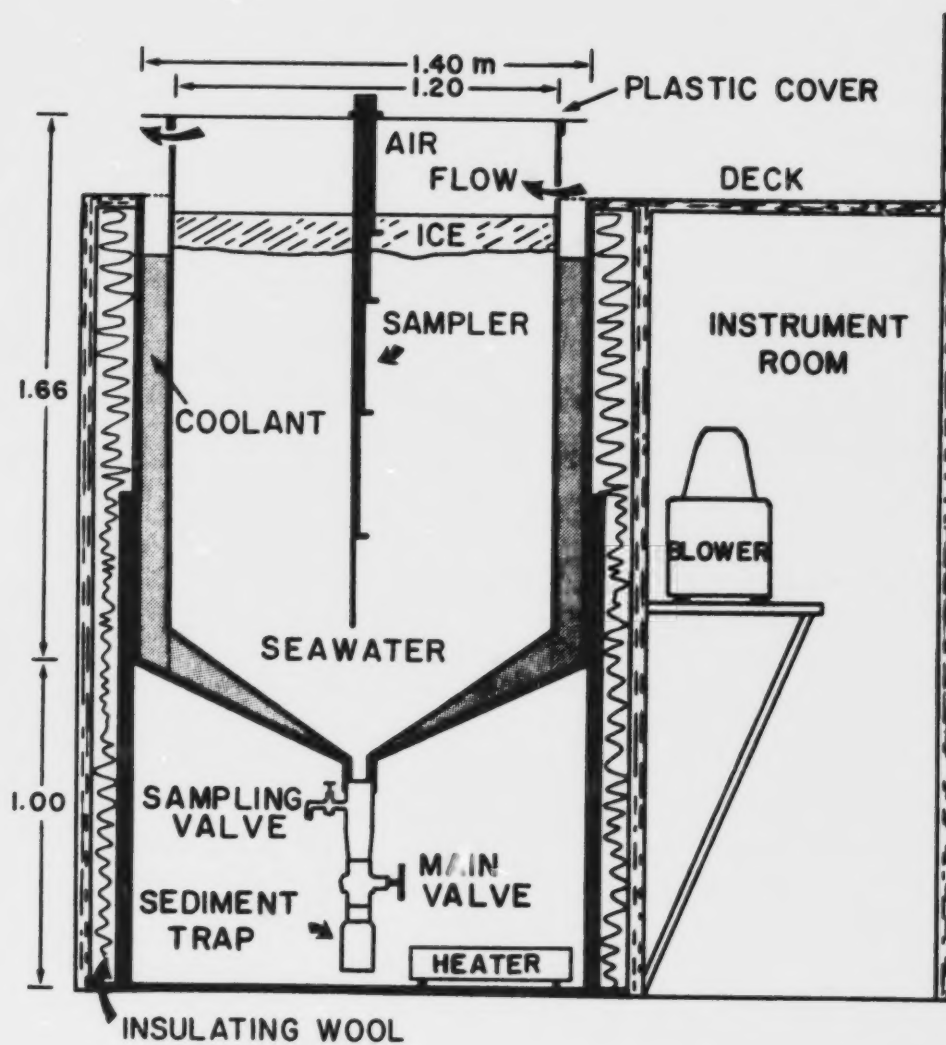


FIGURE 1. SIDE VIEW OF THE SIMULATOR PROTOTYPE USED FOR THE STUDIES OF OIL BIODEGRADATION UNDER THE ICE.

free circulation of a coolant (ethylene glycol and water in the present experiment). The inside wall of the inner cylinder was coated with a white adhesive Teflon film (1.6 mm thick) to avoid metal contamination in the seawater and to ease the final clean-up. The sampling device formed with 5 glass tubes of different lengths and the air bubbler were settled at the center of the cylinder through the plastic cover (Fig. 1). The ambient cold air was circulated over the seawater surface with an industrial vacuum cleaner similar to the blower used for the MNS apparatus developed for testing oil spill dispersants (MACKAY and SZETO, 1980). The main ball valve, the sampling valve, the sediment trap and all fittings were non-corrosive thermoplastic PVC construction. The particles settling from the water column were collected weekly in the sediment trap.

In order to avoid the complete freezing of the water in the simulator during the very cold days of the winter, the apparatus was carefully sheltered with insulating glass wool, the temperature of the coolant was controlled ($+1^{\circ}\text{C}$) with a water bath circulator and extra heat was provided when necessary by a heater fan located at the bottom section of the simulator. The temperature of the seawater was monitored daily with an immersion probe ($+0.05^{\circ}\text{C}$) attached to the sampler.

The inner cylinder was filled with 1675 L of unfiltered seawater ($\text{S}^{\circ}/\text{‰} = 28.0$) and the air flow was turned on. Twenty-four (24) hours were allowed for the settling of the fine particules from seawater and the temperature equilibration in the whole apparatus. The Western Sweet Blend crude oil (565 mL) provided by Environment Canada was added to the surface of seawater with Corexit 9527 (56.5 mL) following the procedure proposed by MACKAY and SZETO (1980) for dispersant testing. Seawater was sampled at different depths on days 0, 1, 2, 4, 8, 11, 15, 20, 28, 40, 50, 60, 70, 81, 102, and 125 for the measurements of the oil content and the chromatographic separations. The amount of oil in each sample (200 to 500 mL following the expected concentration of oil) was determined by the spectrophotometric method proposed by MACKAY and SZETO (1980). The oil extracts were concentrated and separated on a two-step microcolumn of silica gel and aluminium oxide, and then gas chromatographed following a procedure adapted from DESIDERI *et al.* (1984) and FOGHT and WESTLAKE (1982). Gas chromatography was carried out on a Varian (model 3400) with a 30-m bonded phase capillary fused silica column (DB-1 for saturates and DB-5 for aromatics) and an on-column injector. Seawater samples were also taken weekly for bacteria counts and nutrients determinations (nitrogen and phosphorus).

OBSERVATIONS AND RESULTS

1. Temperature control

The main expected difficulties with such a simplistic apparatus were related to the temperature control of the seawater into the simulator. The following tasks were pointed out at the beginning of the experiment:

- a) get the ice formation on the seawater surface as soon as possible,
- b) avoid the presence of ice on the inner cylinder wall and in the sediment trap,
- c) imperatively avoid the complete freezing of the water column, and
- d) preserve the ice cover for many months.

The simulator prototype shown in Figure 1 was found very efficient to fulfill most of these tasks. The Figure 2 summarizes some physical and microbial parameters observed into the simulator. The ambient air temperature ranged from -30°C in the coldest nights of January to over 10°C during the warmest days of March. The average night temperature was always below 0°C with exception for few days at the end of January (days 65 to 68 in Figure 2) were an unusual warm weather caused the ice melting into the simulator. The variation of the seawater temperature is shown in the top section of the Figure 2 whereas the presence of the ice cover is denoted by the continuous thick line in the bottom section of the same figure. The ice appeared twenty-four (24) days after the beginning of the experiment and was present most of the time during the following one hundred (100) days.

2. Microbial activity

The microbial degradation of chemically dispersed crude oil has been studied by many authors (CRETNEY *et al*, 1981; FOGHT and WESTLAKE, 1982) but, to our knowledge, such a study has never been reported for a long-term experiment with seawater temperature near or below 0°C . In the present study, it was intended to evaluate the effects of the low temperature on the natural bacteria population growth and on the rate of the oil degradation. The bacteria concentration (log scale) observed into the simulator is reported in the Figure 2. The natural concentration level found in the St. Lawrence Estuary in November was very low ($300\text{--}400$ units/ cm^3) nevertheless the population grew quite rapidly in presence of dispersed oil in spite of the prevailing low temperature which shows the excellent adaptation capability of these microorganisms to severe conditions. As the simulator was a closed system, nutrients were supplemented in order to maintain the concentrations found in the estuary (nitrates = $15\text{--}20$ nmol/ cm^3 and phosphates = $1\text{--}2$ nmol/ cm^3). Twenty (20) days after the formation of the ice cover a major decrease of the dissolved oxygen concentration was observed due to the absence of air-water exchanges and it was decided to bubble air slowly below the ice to avoid anoxic conditions and the probable collapse of the bacteria population. The growing rate was strongly improved by the air bubbling and the population reached $250\text{--}300 \times 10^3$ units/ cm^3 from day 80 to the end of the experiment. This concentration seems to be the maximum achievable level.

3. Oil dispersion and weathering.

The initial oil dispersion by means of Corexit 9527 was very efficient and over 90 % of the oil added to the seawater surface was found in the water column after six (6) hours and only few

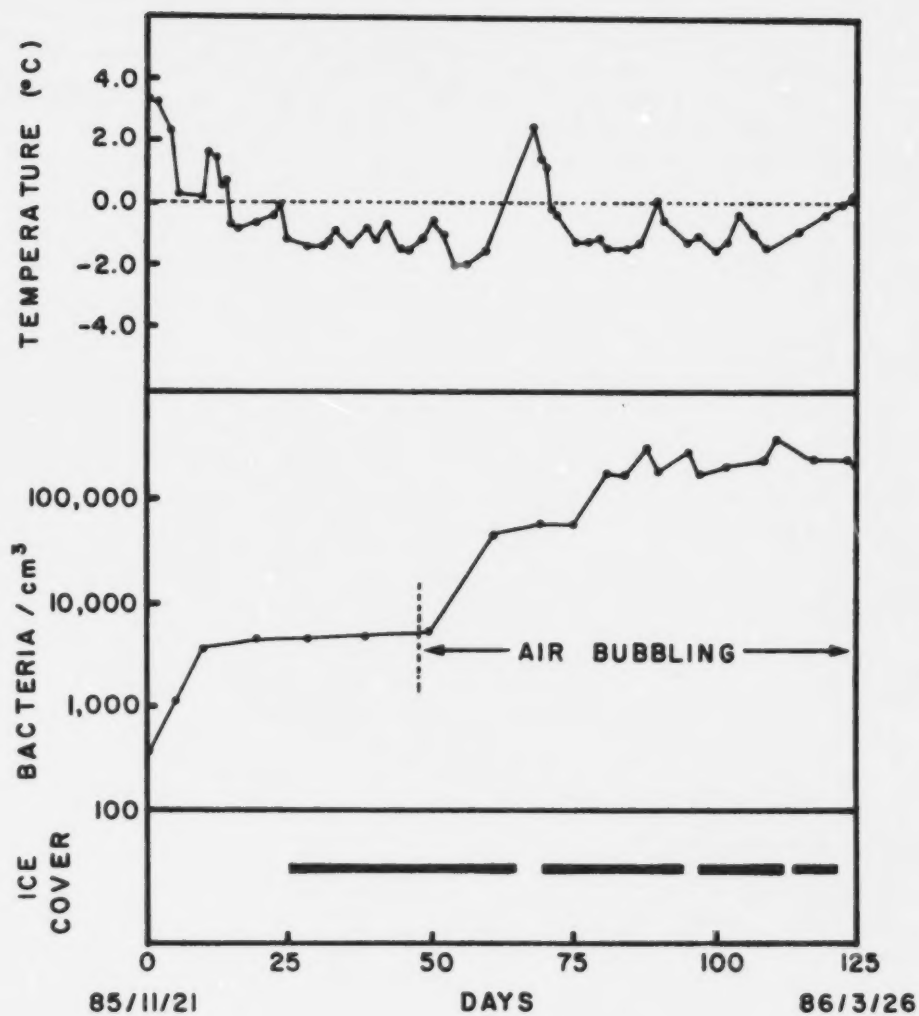


FIGURE 2. THE TEMPERATURE VARIATIONS OF SEAWATER, THE BACTERIA CONCENTRATION AND THE ICE COVERAGE OBSERVED IN THE SIMULATOR FROM NOVEMBER 21th, 1985 TO MARCH 26th, 1986.

small chocolate mousse patches were apparent at the surface. The Figure 3 shows the oil concentration measured just below the surface (10 cm) and near the bottom. The percentage of dispersed oil as estimated from the average oil concentration observed in the water column is also reported. These results shows the rapid lost of the oil from the water column since only 25 % (w/w) of the initial oil was still present in seawater after twenty (20) days. This behavior can not be attributed to the microbial degradation as the bacteria count was very low for the same period (Figure 2). We observed two processes:

- 1) The slow resurfacing of the oil droplets and the formation of larger mousse patches under the action of the air circulation over the first twenty (20) days.
- 2) The precipitation of thin beige particules presumably produced by the microbial activity. These particules were carrying down micro-droplets of partially degraded oil.

These weathering processes are illustrated by some selected gas chromatograms of the saturate fraction shown in Figure 4. The chromatograms 1 and 2 show clearly the biodegradation occurring in the water column over a period of 101 days. The isoprenoids pristane (Pr) and phytane (Ph) remain present while linear alkanes (C_{16} , C_{18} , and others) have almost disappeared. The chromatograms 3 and 4 show interesting changes in their general patterns of alkanes distribution. The profile 3 seems to indicate a selective biodegradation of light alkanes on the oil extracted from particules found in the sediment trap whereas the profile 4 shows the absence of biodegradation on the chocolate mousse even after 125 days. In the latter case, the lighter alkanes have been lost mainly by evaporation and the ratio C_{18}/Ph is closed to the same ratio observed in the profile 1. Observations on the inclusion of dispersed oil droplets into the ice sheet and the biodegradation of the aromatics will be reported elsewhere.

IMPROVEMENTS AND DEVELOPMENT

The overall cost of the simulator prototype was less than seven (7) thousands canadian dollars (1985 prices) which includes the water bath circulator and the immersion temperature probe. The prototype fulfilled the main task of the project (as presented in the introduction) and only few technical problems have been encountered. The following improvements are suggested:

- 1) The air flow generated by the vacuum cleaner was not enough powerful to create surface waves and only ripples were formed. Two blowers should be used in tandem.
- 2) As the circulation water bath was not equipped to refrigerate the coolant, it became impossible to avoid the ice melting when an unexpected warm weather occurred at the end of January. A cooling unit should be added to the circulation system.
- 3) It became very difficult to sample seawater from the top of the simulator when the air temperature went down to $-10^{\circ}C$ as seawater froze instantly in the glass tubing. The sampler concept has to be reviewed and improved.

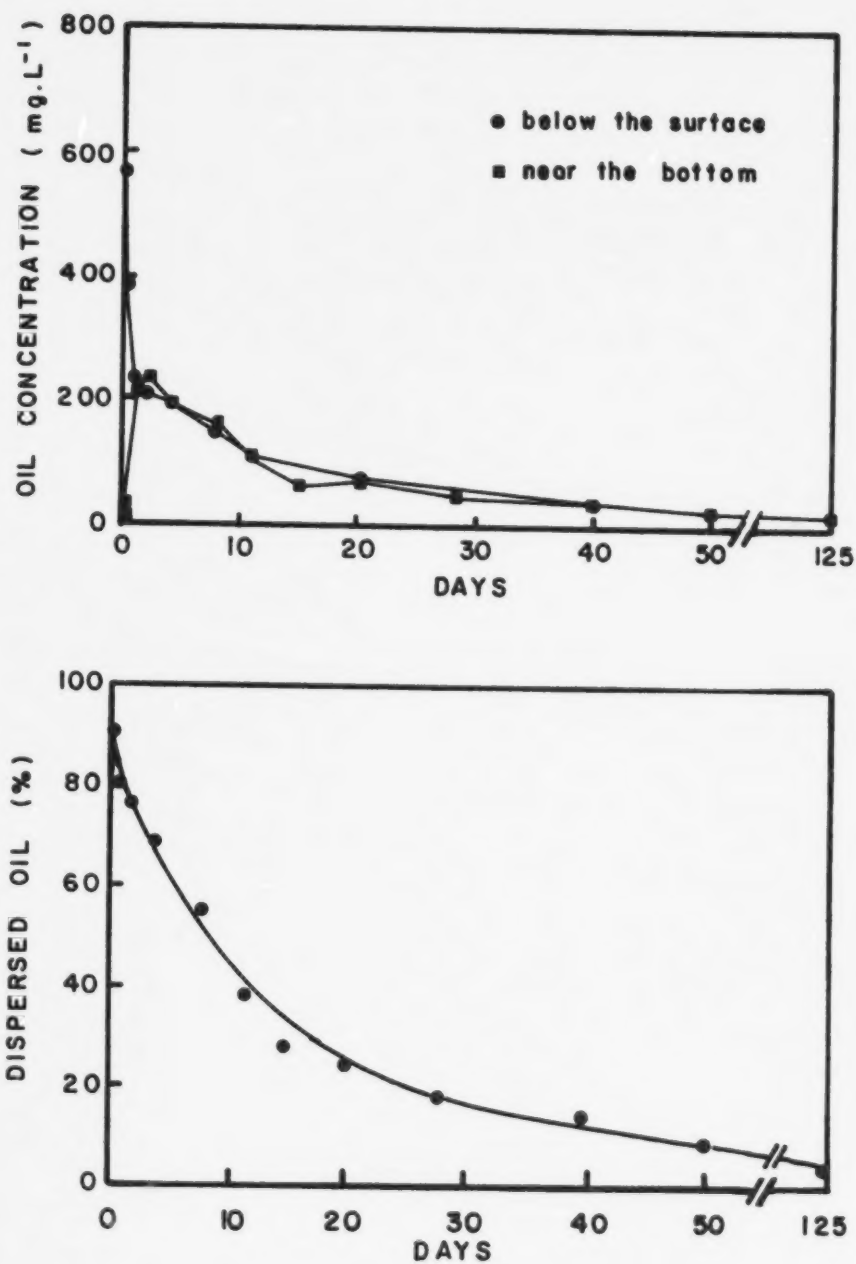


FIGURE 3. THE OIL CONCENTRATION IN THE WATER COLUMN AND THE PERCENTAGE OF DISPERSED OIL OBSERVED IN THE SIMULATOR.

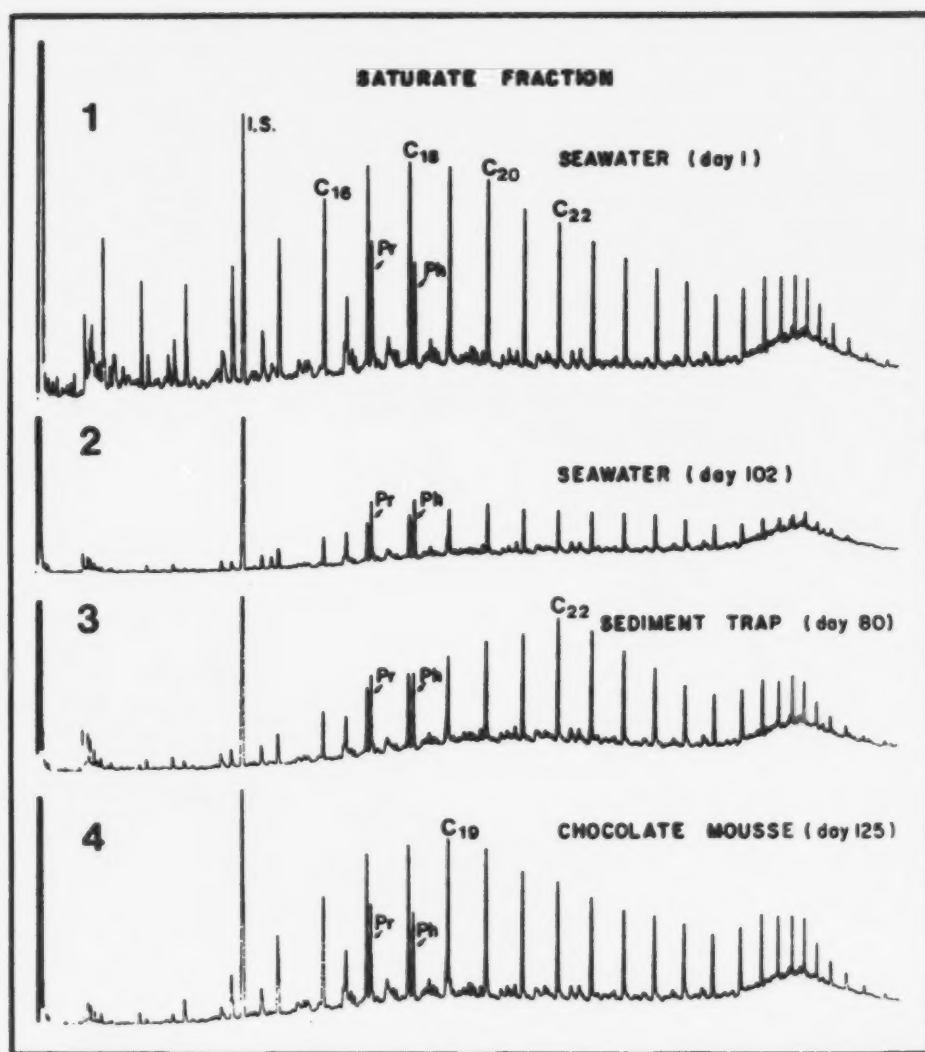


FIGURE 4. SOME CHROMATOGRAMS SHOWING THE WEATHERING PROCESS OF THE CRUDE OIL (SATURATE FRACTION ONLY) IN THE SIMULATOR. Pr = PRISTANE, Ph = PHYTANE and I.S. = INTERNAL STANDARD (HEXAMETHYL BENZENE).

The simulator can also use freshly pumped seawater from our wet laboratory as coolant during the warm months which allow us to run experiments (mainly chronic toxicity tests and long-term dispersant effectiveness) at temperatures closed to the actual seawater temperature observed in the St. Lawrence Estuary. Tested benthic organisms with or without sediment can be settled on a grid placed on the conical bottom of the inner cylinder. A project for the build-up of five simulators (2000 L each) in a row is now on the way. Such a system should allow the simultaneous testing of many physical, chemical and biological parameters under severe conditions encountered during fall and winter.

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LONG-TERM PERSISTENCE OF BUNKER C FUEL OIL AND REVEGETATION OF A
NORTH-TEMPERATE SALTMARSH: MIGUASHA 1974-1985.

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INTRODUCTION

Low-energy mariane coastal environments are generally considered to be highly susceptible to long-term persistent contamination from coastal oilspills because self-cleaning by wave action and tidal flushing is very low, and because the spilled hydrocarbons tend to become entrapped in depressions and within beach interstices.

These processes have been documented for several such environments (Vandermeulen and Gordon, 1976; Baker et al., 1984; Vandermeulen et al., 1981). Within this context, saltmarshes and other coastal wetlands are particular problems because traditional cleanup or countermeasure operations (booming, manual or mechanized cleanup) invariably aggravated the problem, either by forcing more of the spilled oil into the wetland sediments or by drastically damaging the wetland ecosystem.

One alternative to oil spill cleanup, in the special case of wetlands, is a nil response in which the spilled oil is left untouched in the marsh, and is left to natural albeit very slow natural weathering and decomposition processes. The oiling and subsequent setting aside of the oiled saltmarsh near Miguasha, Quebec, provided an opportunity to monitor the long-term fate of such an uncleaned marsh environment. The present paper documents persistence of stranded eleven-year old Bunker C oil, and the revegetation of marsh areas impacted by the spilled oil in 1974.

MATERIALS AND METHODS

Vegetation surveys and sediment sampling were carried out in September 1985. In addition to the original test plots laid out in 1975, three transects were laid out across the marsh, with sampling stations marked out along them (Figure 1).

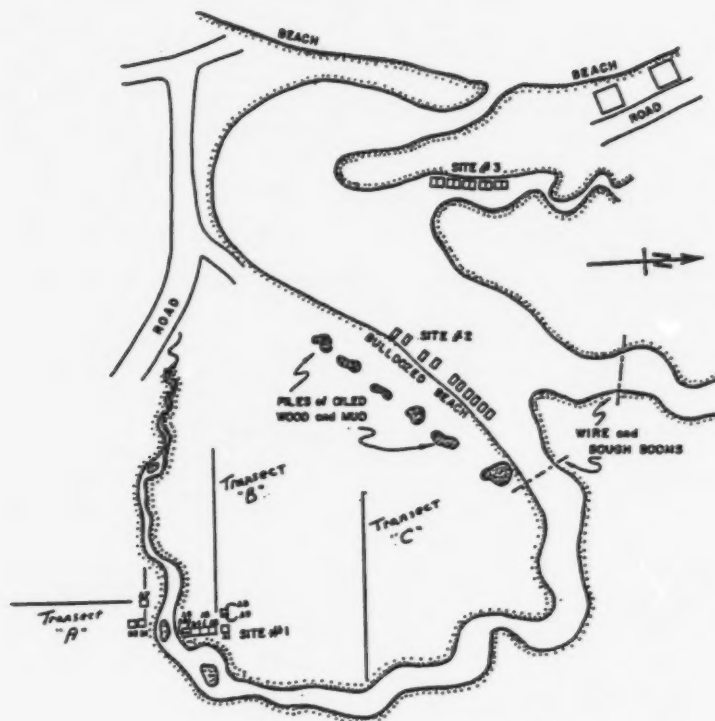


Figure 1. Schematic representation of Miguasha saltmarsh showing location of 1975 test plots, and of the 1985 vegetation transects.

Vegetation Surveys

Vegetation was studied using a 1 M^2 quadrat, divided into 100 $10 \times 10 \text{ cm}^2$ squares. Species composition, rooted frequency, and percent cover were inventoried for each sample. Each of the original test plots were sampled in this way, as well as were stations along the three transects. The data were then analyzed objectively by quadrat, regardless of their location in the marsh. For identification of quadrat number, see Table 1. Data were averaged for the species within each sample, and the averages were relativized to obtain importance values (IV's). Multivariate analysis was done using Decorana (Hill, 1979a) and Twinspan (Hill, 1979b). Both methods group individuals according to their similarities, Decorana providing a graphic presentation, application of Twinspan resulting in a two-way table. Statistical analyses were performed on the CDC Cyber at Acadia University.

Hydrocarbon Analysis

Both surface (0-2cm) and subsurface (-2cm) sediment samples were collected into hexane-rinsed glass sampling jars, and stored frozen

(-10°C) until extraction and analysis.

Sediment aliquots were extracted by alkaline digestion, and partitioned into n-alkane solvents. Quantitative analysis was by UV-fluorescence (UV/F) (310nm excitation, 374nm emission), with results expressed as oil equivalents using a sample of buried Bunker C as reference material. Qualitative analysis was by the method of Lloyd (1971), using synchronous excitation-emission UV/F scans and peak-height analysis as detailed in Vandermeulen et al. (1981). Glass capillary-chromatography was done on aliphatic and aromatic fractions (F1, F2) (HP-5730A), following liquid chromatographic separation

All solvents used in sediment-hydrocarbon analysis were double distilled in glass from ACS-grade reagent stock.

SPILL BACKGROUND

On September 14, 1974, the tanker Golden Robin ran aground in the Baie de Chaleur, just off Dalhousie, New Brunswick. The Baie forms the mouth of the Miramichi estuary which marks the border between New Brunswick and the province of Quebec. At this point the estuary is approximately 2 km wide. Approximately 1,000 barrels (159,000 litres) of Bunker C fuel oil were spilled into the estuary, resulting in extensive intertidal oiling of both the New Brunswick and opposite Quebec shorelines.

In the course of this, the small marsh of Miguasha, located on the Quebec side of the estuary, became oiled also. Despite efforts to contain the incoming oil within the mouth of the main marsh drainage channel by booming off two small secondary marsh channels, a substantial but undetermined amount of spilled Bunker C oil reached the marsh interior. During subsequent high tides the oil spilled over the banks onto the adjacent high marsh vegetation. Oiling of the marsh itself was not extensive, and was restricted largely to lower lying portions of the marsh, and the channel banks.

Although cleanup of the bay was effected immediately, the oiled saltmarsh was left uncleaned until the following spring, 1975. Several cleanup approaches were attempted, primarily in the back portion of the marsh where oiling had been heaviest and where spilled stranded oil and oiled vegetation was still very much evident. These included manual removal of oiled vegetation, digging and spading of oiled vegetation and surface sediment layers and various burning methods, as well as mechanized plowing and removal of oiled sod with a motor-driven sod-cutter (Table 1, Figure 1). None of the methods was highly successful, and the mechanized methods especially disturbed the marsh sediment greatly. Results are summarized in Cejka (1975).

A subsequent field survey, and chemical analysis of sediments from the various testplots, done in 1976 and 1977, revealed chronic poor recovery of vegetation in all test plots, and the presence of varying large amounts of hydrocarbons within the sediments (Vandermeulen and Ross, 1977). In all test plots, hydrocarbons had penetrated to at least 10 centimetres, and in some down to 20 cms.

Table 1. Marsh test plots and 1975 test treatments. For location of test plots refer to Figure 1.

Test plot	Condition in 1974	Treatment in 1975
A1	Oiled	non-cleaned control
A3	Oiled	manual cleanup
A4	Oiled	cleanup by cutting and removing vegetation
A5	Oiled	cleaned by burning with propane torches
A6	Oiled	burned with varsol
A7	Oiled	burned with gas/No.2 fuel oil mixture
A8	Oiled	digging out oiled sod with spade
A9	Oiled	removal of oiled sod with hand-saw
B1	Oiled	sodcutter
B2	Oiled	plowed with farm plow

RESULTS

General Marsh Vegetation

1. General Marsh Morphology

The Miguasha saltmarsh is located on the north shore of the Baie de Chaleur, across from Dalhousie, New Brunswick. The marsh is small, ca. 1 km², and lies protected behind a gravel spit. It is drained by a simple drainage network of two small secondary channels which drain into a single main channel. In the absence of freshwater stream input, main water input from the landward side is by surface runoff from the surrounding more elevated land, a mixture of farmland and pine/spruce forests.

The front part of the marsh bordering the main or primary channel is in fact well above mean high tide, formed of sand deposits that are overgrown with typical dune vegetation.

The typical marsh environment is found in the back portion of the system, drained by the secondary channels, and constitutes a typical Atlantic coast marsh, with characteristic and visually distinct vegetation zones. Zone 1, at the water's edge and along the edge of marsh drainage channels, was dominated by generally pure stands of Spartina alterniflora. Zone 2, evident just above zone 1, was dominated by Spartina patens. This zone also contained occasional Arenaria lateriflora, Plantago maritima, Limonium nashii, Salicornia europaea, Suaeda maritima, Atriplex patula, and Glaux maritima. Zone 3, well away from the water's edge, was co-dominated by Plantago maritima and Glaux maritima, with occasional Suaeda maritima and Salicornia europaea. Solidago sempervirens was relatively rare, found primarily on raised hummocks immediately beside the drainage channels. Marsh pannes on the

upper marsh often contained a luxuriant growth of Ruppia maritima.

2. Vegetative Recovery

Overview 1975-1984

Photographic documentation of the test plots, first oiled in 1974 and subsequently subjected to various cleanup trials in 1975, show very heavy oiling of all vegetation, with both cleanup crew and equipment mired in masses of oiled vegetation and surface sod.

Observations made during 1976 and 1977 field trips showed dry deposits of tar over the various test plots, generally in the form of an asphaltic layer of from one to several cms in thickness, and generally broken up by drying and cracking into circa one decimeter square flakes. The two test plots that had been either dug out (A8) or had the sod removed with a hand-saw (A9) were both filled with water, with tar submerged.

Over the subsequent period, 1978-1984, vegetation gradually reinvaded the various test plots. The process was most rapid in the test plots that had been treated either manually (A3, A4) or by burning the oiled vegetation (A5, A6, A7). By 1984 the vegetation in these plots, and in the two plots treated with sodcutter (B1) and farm plow (B2) appeared visually restored, and not differing from the surrounding vegetation. The exceptions were the two test plots A8 and A9 which had had the surface sod removed by either digging or hand-cutting. In both of these revegetation was slow, and from a distance the vegetation appeared more yellow in color than vegetation in adjacent test plots, or in surrounding non-oiled areas.

At the same time the areas of dried tar residue disappeared from view, mainly by slow invasion of marsh vegetation. One extensive oiled area remained evident for several years, but had disappeared from view during a four-year period (1978-1982) when no visits were made to the marsh.

1985 Survey

Of the various test plots marked out in 1975, the general locations of plots A1 through A6, A8 and A3 were relocated. Test plots B1 and B2 were no longer identifiable, or distinguishable from the surrounding marsh. Test plot A7, originally located on the edge of a secondary drainage channel, was not identifiable by vegetative abnormalities per se. However, the bank of the drainage channel at this point was marked by a discharge of greyish-white material that had been noted on previous visits, which served to identify the location of A7.

Only one test plot, #A7 (quadrat 7 in the numerical analysis), was markedly different from its surroundings. The vegetation and surface root mass in this plot had, in 1975, been dug out with a spade to a depth of several centimeters. At the time of sampling for the present study, 1985, the test plot was a small pond, with Spartina alterniflora along its edges.

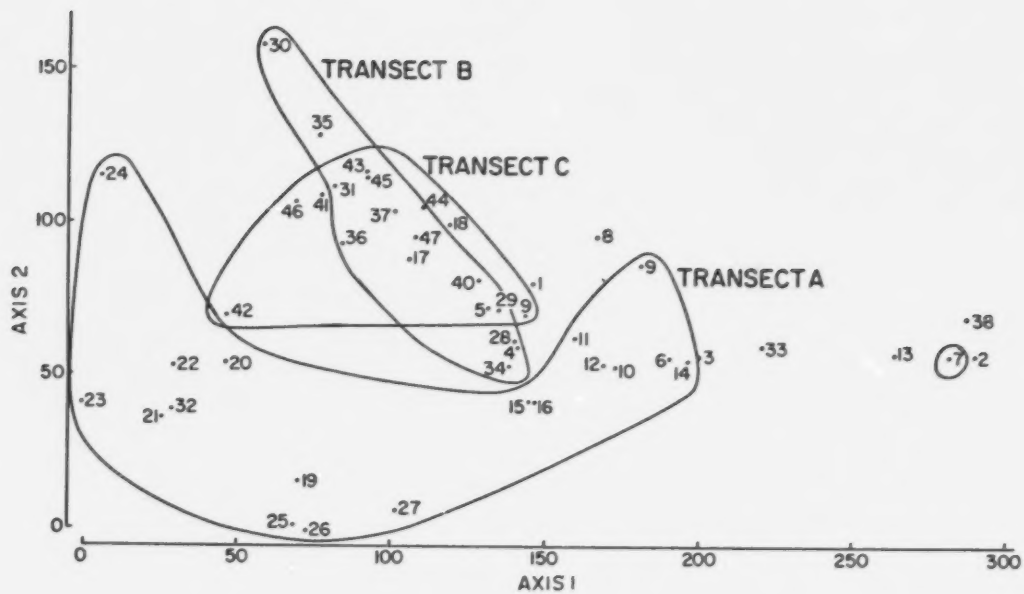


Figure 2. Decorana ordination of the vegetation data from the Miguasha salt marsh. Forty seven quadrats are shown, clustered according to their floristic similarities. The axes are mathematical abstractions, determined by Decorana.

Table 2. Twinspan analysis of the vegetation data from the Miguasha salt marsh. Quadrat numbers (1-47) are along the top, and species names are on the left. The values in the matrix show relative importance of species. The dichotomous divisions made by Twinspan are shown for species on the right, and for quadrats along the bottom.

[illegible]

The vegetation survey data were assembled into a matrix of relative importance values. Analysis of these data using Decorana resulted in the ordination shown in Figure 2. Tidally inundated quadrats dominated by Spartina alterniflora are found on the extreme right (#2, 7, 13, 38), while Glaux dominated high marsh quadrats are grouped on the extreme left (#21, 22, 23, 24, 32, 42). Between these extremes, Spartina patens dominated quadrats tend to lie on the right, and Plantago maritima quadrats on the left. Hence the first axis is similar to the initial zonation visualized before the analysis, except that here the Glaux maritima quadrats were separated from the Plantago maritima quadrats, which was not visually apparent in the field. Most of the quadrats from the various 1975 test plots were similar to surrounding quadrats, and quadrats from similar areas generally grouped together. The exception was quadrat 7 (1975 test plot A8) which grouped with the S alterniflora dominated plots 2, 13 and 38.

Table 2 shows the two-way table produced by the Twinspan analysis on the same data. The hierarchical divisions on the quadrats are shown along the bottom, and the divisions on the vegetation species are shown

along the right. Generally the groupings are similar to those from the Decorana ordination. Again quadrat 7 is grouped at the far right, among the plots dominated by S. alterniflora. The only anomaly is quadrat 9, which is clustered with quadrat 38 on the same branch in Table 2, but is separate from #38 in Figure 2. Quadrat 38 was located on the bank of the main secondary drainage channel in this portion of the marsh, and was dominated by S. alterniflora. The Twinspan diagnostics indicated that #9 and #38 were clumped together mainly by the total absence of Glaux maritima and Plantago marina.

3. Hydrocarbon Survey

Hydrocarbon Characterization

Qualitative examination by UV/F synchronous scanning (SEES) revealed the usual UV pattern expected with a bunker C contaminated sediment, with a major peak at 360nm, pronounced fluorescence at 380 nm and 408 nm, and tailing off subsequently to near zero at 480 nm. The latter region, 380 nm and above, corresponds to the fluorescence response region for 5-ring compounds and larger (Lloyd, 1971). This characteristic pattern was found in samples of buried Bunker C deposits, and in several surface and sub-surface sediment samples (top trace, Figure 3).

Most sediment samples, however, elicited a differing SEES profile. While generally resembling that of standard whole oil with the major fluorescence peak at 360 nm, these differed in a markedly lower fluorescence response above 360 nm, corresponding to reduced numbers of 5-ring and larger aromatic hydrocarbons (middle traces, Figure 3).

A third and differing SEES profile was found in a number of samples, primarily in deeper subsurface sediments and in remote unoiled areas of the marsh. In these the main fluorescing region was shifted to the left, with a major peak at 347 nm that was either equal to or dominated the diagnostic hydrocarbon peak at 360 nm (bottom trace, Figure 3). SEES scans of such samples also frequently showed pronounced peaks at 432nm and 457 nm. These differences were quantified and confirmed using the peak-height analysis of UV/F SEES scans that has been described elsewhere (Vandermeulen et al, 1981).

GC-chromatograms of the F1 (aliphatic fraction) and F2 (aromatic fraction) of a buried Bunker C sample showed a highly degraded pattern of peaks overlying a large unresolved envelope, consistent with the weathering of stranded oil for several seasons (Figure 4). Similar GC analysis of sediments that had been indicated as contaminated by UV/F analysis also showed such patterns, with a large unresolved envelope underlying a pattern of peaks consistent with the continued presence of n-alkanes and aromatic hydrocarbons.

Hydrocarbon Concentrations

Quantitative examination by UV/Fluorescence (310 nm excitation, 374 nm emission) of sediment samples extracted for hexane solubles suggested widely varying concentration of fluorescing materials, presumed to be hydrocarbons, in all samples. Levels varied between 48.6 ug/gm in a

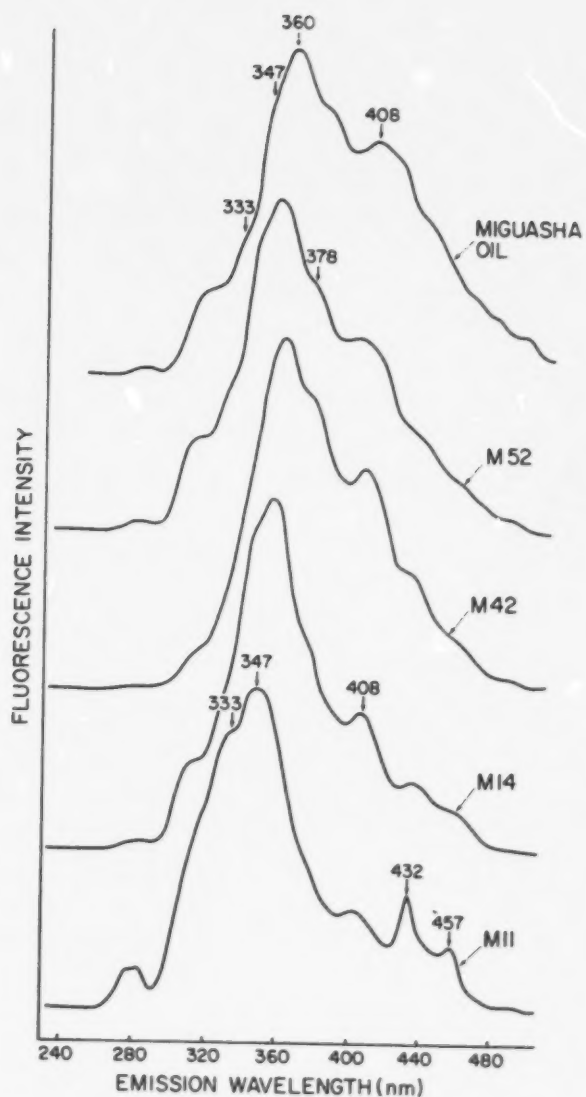


Figure 3. Simultaneous excitation-emission scans (SEES) of Miguasha buried oil, heavily tarred sub-surface sediments (M52), contaminated surface sediment (M42), newly deposited sediment (M14), and a -20 cm sub-surface sediment (M11).

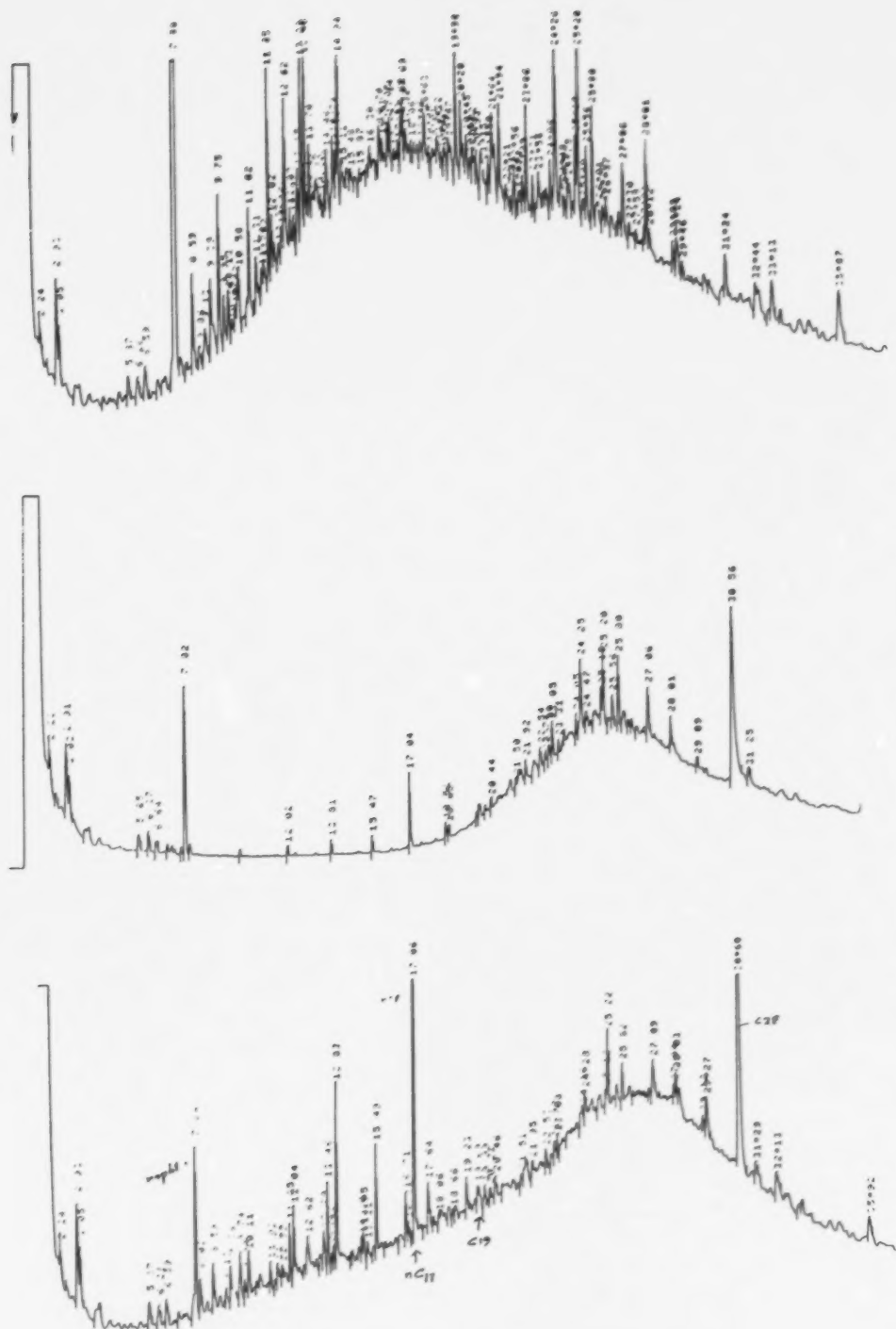


Figure 4. Gas chromatograms of F1 fractions from new sediment overlying a buried tar layer (top), surface sediment sample near oiled region (middle), and from buried tar layer (bottom). (Peaks at 7.8 and 30.6 are internal standards.)

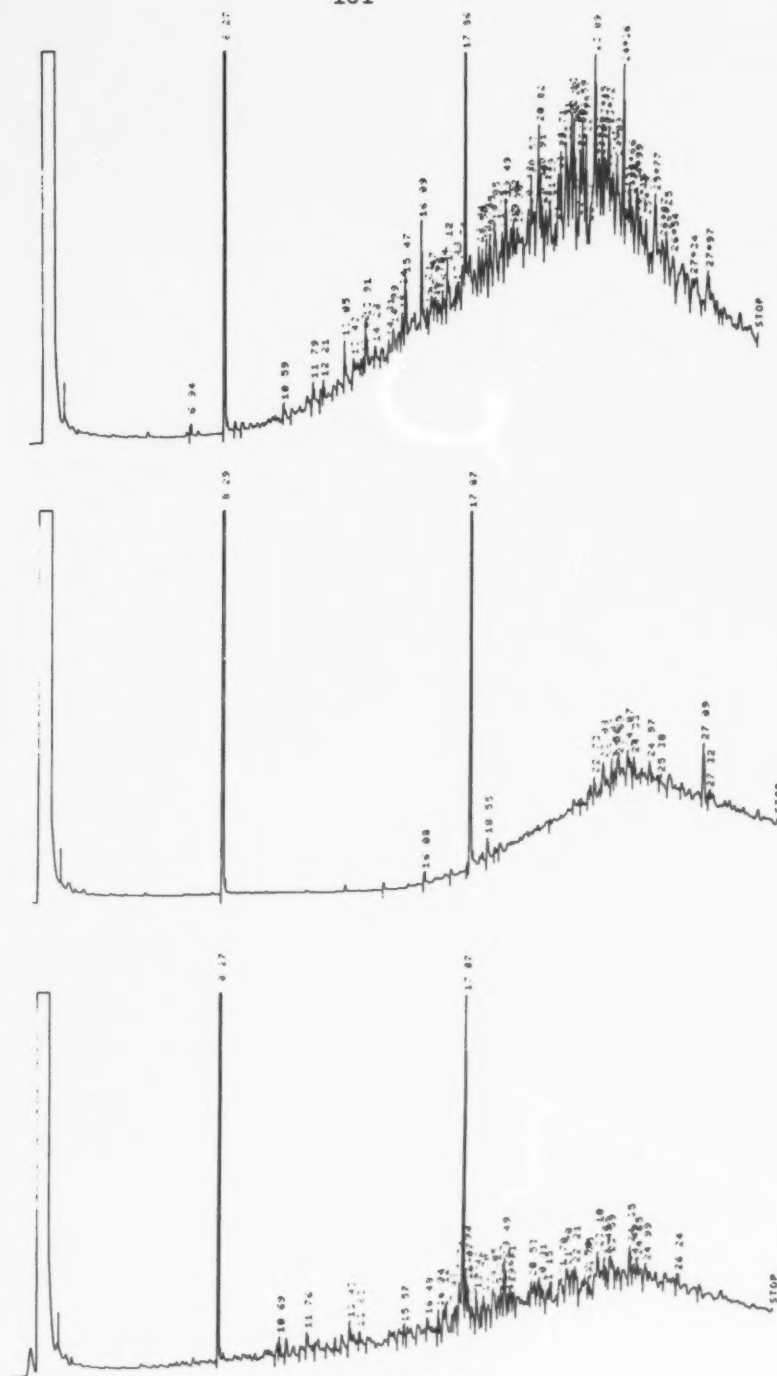


Figure 4 continued. Gas chromatograms of F2 fractions from new sediment layer overlying a buried tar layer (top), surface sediment sample near long-term oiled region (middle), and from buried tar layer (bottom). (Peaks at 8.2 and 17.8 are internal reference standards).

Table 3. 1985 sediment oil equivalents (ug/gm), determined by UV/Fluorescence, in 1975 test plots in Miguasha marsh. Values shown represent total fluorescing materials, and are not corrected for native, indigenous fluorescence. Values marked * judged to be background values, based on UV/F SEES spectra.

				Core depth		
				0-5cm	5-10cm	10-20cm -20cm
Quadrat 1	1975 test plot	A1	1,125.3	1,776.3		
2		A2	340.5	3,621.9	3,188.7	359.6*
5		A6	1,354.9			144.2*
5B			435.6	21,180.3*	384.2*	
6		A7	1,941.8			48.6*
6B			703.4			61.3*
8		A9		6,805.8		

Table 4. Hydrocarbon equivalents (ug/gm) in sediment samples from transect A in Miguasha marsh, September 1985. Determinations by UV-fluorescence represent total fluorescence, and are not corrected for native fluorescing materials. Values marked * judged background from UV/F SEES spectra.

Transect station	A(0-5cm)		B(0-5cm)	
A7-1	1941.8	48.6* (-20cm)	703.4	61.3* (-20cm)
A7-2	399.7		1557.8	
A7-3	319.0		369.7	
A7-4	392.4		177.7	
A7-5	544.7		516.3	
A7-6	508.7		457.6	
A7-7	1793.2		3142.5	
A7-8	156.5		424.8	
A7-10	109.7			
A7-13	226.6			
A7-15	558.6			

- 20cm sediment sample to 58,697 ug/gm in a sample of buried tar deposit. Most samples varied between 150 to 10,000 ug/gm.

Representative fluorescence intensities for extracts from sediments from the 1975 test plots, resurveyed in 1985, are shown in Table 3. Surface and near surface sediments generally ranged between 340 and 6806 ug/gm oil equivalents. One sample, taken from 5-10cm in test plot A6, was an anomaly at 21,180 equivalents. Deeper, -20cm, sediments

generally ranged between 49 and 360 ug/gm oil equivalents.

Representative values for oil equivalents from one of the main marsh transects, transect A originating from 1975 test plot A7, are shown in Table 4.

DISCUSSION

Most of the 1975 test plots appeared indistinguishable from the surrounding marsh areas, and this was supported by the analyses of the vegetation surveys. However, there were some analytical problems that could have been overcome if the test plots had been selected slightly differently in 1975. A major problem was that the cleanup or test plots were not blocked originally to allow for vegetation zonation. Second, no initial plant inventory was taken. And third, there were no replicate plots, so that no statistical analysis was possible. Hence, no detailed conclusions may be drawn about the succession of vegetation after the oil spill or after the subsequent cleanup trials.

No morphometric data were collected in 1985, but as pointed out, the vegetation appeared normal, consistent with that in other salt marshes at that time of year. Except for test plot 7, there were no visible outlines of any of the old test plots, and vegetation was continuous throughout the marsh. The one exception to this was test plot A8 (quadrat 7), located on the high marsh, but which was dominated by Spartina alterniflora. The latter is characteristic of low marsh areas that are regularly inundated by saltwater. This test plot had been used in 1975 to assess the usefulness of digging out and removing oiled sod mass, lowering the level of the marsh back to the S. alterniflora level. The vegetation for this particular location was therefore normal in terms of its zonation, although it was surrounded on all sides by S. patens.

The value of the numerical analyses was in the association of similar plots based on floristic composition. The test plots treated with cleanup procedures were not outliers from the non-treated test plots. Their relative position with respect to other areas in the analyses correlated well with their actual location in the marsh, with the obvious exception of test plot A8. That is, there were no unexplained anomalies between the perceived zonation and the subsequent analysis.

From an oiling point of view, the 1975 test plots remain foci of ongoing hydrocarbon contamination for the marsh. In this respect the data from UV/Fluorescence is used primarily to screen extracts for presence of hydrocarbons or for native fluorescing material, in particular using the SEES profiles. The presence of large amounts of native fluorescing materials in the marsh sediments, e.g. plant pigments, becomes a significant interfering factor in these fluorescence data, especially where hydrocarbons are present in low concentrations. While in regions of high concentrations, such as in surficial oiled sediments, the oil hydrocarbons over-ride fluorescence due to native materials, this becomes less significant as the concentration of oil hydrocarbons relative to native pigments decreases. We suspect in fact

that in table 3, the value of 21,000 mg/gm reported for the -5/-10 cm sample for quadrat 5B is due largely to background fluorescence, based on the presence of the dominant background fluorescence maximum at 347 nm which is found to be characteristic of native fluorescence. Similar SEES spectra were also found in the -20 cm samples for quadrats 2, 5, 6 and 6b, which are all relatively free of hydrocarbons when examined by GC.

It is interesting to note, however, that most of the profiles for the surface sediments indicate deficiencies in 5-ring and larger aromatic materials (decreased peak intensities above 360nm) when compared with SEES profiles on whole Bunker oil. Instead, we see a predominance of lower molecular weight, one to three and four ring, materials. This suggests that much of the present surficial contamination may be the result of water-borne cross-contamination.

In sub-surface sediments, hydrocarbons continue to persist in the original oiled areas, but are rarely found in large amounts below 15 cm. Even in heavily oiled areas there was little evidence of high concentrations, except where strata or zones of intact oil or oiled vegetation had become buried by subsequent siltation and marsh buildup.

Most remarkable was the finding of the buried oil layer along Transect B. The circumstances suggest that this particular region of the marsh was and remains an area of rapid sediment deposition and marsh growth. This also suggests that under certain conditions of high sedimentation rates the easiest and least damaging countermeasure approach to oiling of a saltmarsh may be to simply leave the marsh to natural revegetation.

In terms of marsh recovery by revegetation, the overall impression from the long-term followup suggests two processes were at work here. The first consists of two stages - weathering of the stranded oil slicks with concomittant impregnation with sediment, followed by reinvasion by marsh vegetation. The latter originates either from already existing rootmasses under the weathered tar layer, or by lateral reinvasion. The latter has also been observed at the site of the oiled Ile Grande marsh, in north Brittany, France.

The second process consists mainly of total burial by deposition of imported fine sediments over the layer of oil and oiled marsh vegetation. In this case the newly deposited layer of sediment was up to 15 cm in depth, and indicates a high rate of deposition for this region of the estuary. Interestingly, there was no evidence of new vegetation embedded within this new sediment layer suggesting perhaps that new root formation had not occurred until a sufficiently deep sediment layer had been formed over the buried and relatively unweathered oil layer. Certainly no roots of the new marsh vegetation were found to penetrate down into and through the buried oil horizon.

CONCLUSION

The Miguasha saltmarsh has generally recovered, with few signs that either the oil itself or any of the cleanup procedures, except for oiled

sod removal, has either helped or hindered the revegetation.

Sediment samples taken from the initial oiled marsh areas, however, retain significant and identifiable amounts of Bunker C derived hydrocarbons. These are found primarily in the upper 15cm.

Surface sediments generally show low level hydrocarbon contamination consisting mainly of lower molecular weight hydrocarbons presumably transported and redistributed during tidal inundations of the marsh.

In areas of low sedimentation the recovery pattern is that of oil weathering and vegetative invasion. In areas of high sedimentation and marsh buildup, the recovery was by burial of the spilled oil and oiled vegetation layer, followed by subsequent regrowth of vegetation above the subsurface oiled layer.

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EXPERIMENTAL LONG TERM OIL POLLUTION IN A BOREAL ROCKY SHORE ENVIRONMENT

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ABSTRACT

The paper presents the design, experimental range and an overview of the results of a large scale mesocosm experiment performed during 1979 to 1985 at the Marine Research Station Solbergstrand, Eastern Norway. The aim of the experiment was to investigate the effects of continuous sublethal exposure to diesel oil on a cold temperate rocky shore community. The monthly mean temperature range of the mesocosm was 0.6-18.9°C during the 6 years the experiment lasted. The mesocosm communities were established in 1979 by transplantation of rocks with sessile organisms to four flow-through concrete basins (8x5x1.5 meters) equipped with wave generators and tide simulation. The communities were allowed to develop undisturbed for three years, whereafter two of the basins were exposed continuously to a diesel oil in seawater emulsion at mean levels of 130 and 30 µg/liter respectively (fluorescence analysis). The two remaining basins acted as controls. The oil exposure lasted from September 1982 to September 1984. After that the communities were followed for recovery for one year. The experiment covered a range of subprojects aimed at studying the effects on general community structure, community recruitment and metabolism, population dynamics and genetics, physiology, cell chemistry, histology and tissue hydrocarbon levels of key species. The effects ranged from population collapse (blue mussel, amphipods), reduced growth (bladder wrack, kelp, mussels) and recruitment (winkles, barnacles), reduced primary production, increased cover of opportunistic green algae, reduced feeding and energy utilization (mussels, winkles), accumulation of hydrocarbons in algae and animals, to cyto- and biochemical stress indications (mussels, winkles). The effects were in most cases dependent on season. Relation to dose was not always found. The population genetics did not indicate any short term selection due to the oil. After one year recovery, most responses were back to normal, and population regeneration of mussels and amphipods had started, but some physiological dysfunctions were still detected.

INTRODUCTION

Experimental ecosystems or mesocosms have been applied with increasing frequency in pollution research during the last decade. The main strength of such experimental approach lies in the improved realism compared to laboratory tests, and improved possibility of manipulation and of obtaining a desired pollution scenario compared to field investigations. Most mesocosm experiments have been performed on pelagic systems, by use of plastic bags (e.g., Grice & al. 1980, Davies & al. 1980), but benthic mesocosms have also been used successfully (e.g., Bodungen & al. 1976, Kuiper & al. 1983, Oviatt & al. 1982).

Since 1979 four large concrete basins have been used to maintain rocky shore communities at the NIVA Marine Research Station Solbergstrand, Eastern Norway, for the purpose of running experiments on effects of long term, low level, chronic oil exposure. Sheltered littoral rock communities were chosen since such communities are common along the Norwegian coast, and since they are prone to impact by oil pollution. The experiment consisted of two years continuous addition of diesel oil to the basin water, followed by one year recovery from

the oil effects. The purpose was to mimic the pollution scenario found in the vicinity of harbours, marinas or other regions with small chronic oil input to the sea. The experiment covered a multitude of separate subprojects studying aspects from community effects to effects on subcellular functions of organisms.

The purpose of this paper is to give a short description of the mesocosm and experimental design, the oil exposure and environmental conditions, and an overview of the results. Detailed reporting of the component studies are published elsewhere by the authors in charge of these studies.

EXPERIMENTAL DESIGN

Mesocosms

Four rocky shore communities were established in land based concrete basins. Each basin measures 8 x 5 x 1.5 meters and contains 25 m³ of sea water at mid tide (Figure 1). On one side of each basin a wave generator is mounted consisting of a float made of two closed heavy duty PVC pipelines in a steel frame. The float is pivoted at each end and is moved up and down mechanically at 18 strokes per minute creating regular waves which move across the basin to the other side where the main model community is situated. Here four tribunes have been constructed from above high tide to the bottom. The width of each tribune is 42.5 cm and the height is 19 cm. Each tribune is slanted so that the south end lies at the same vertical level as the north end of the tribune below. The basins are supplied with running sea water at a rate of 10 m³/hour to each basin pumped by impeller pumps from 1m depth in the fjord outside the station (from 13m depth in particularly cold winters to avoid ice formation).

From each basin a subsurface outlet leads to a flexible hose with stiff nozzle which is raised and lowered automatically to regulate the basin water

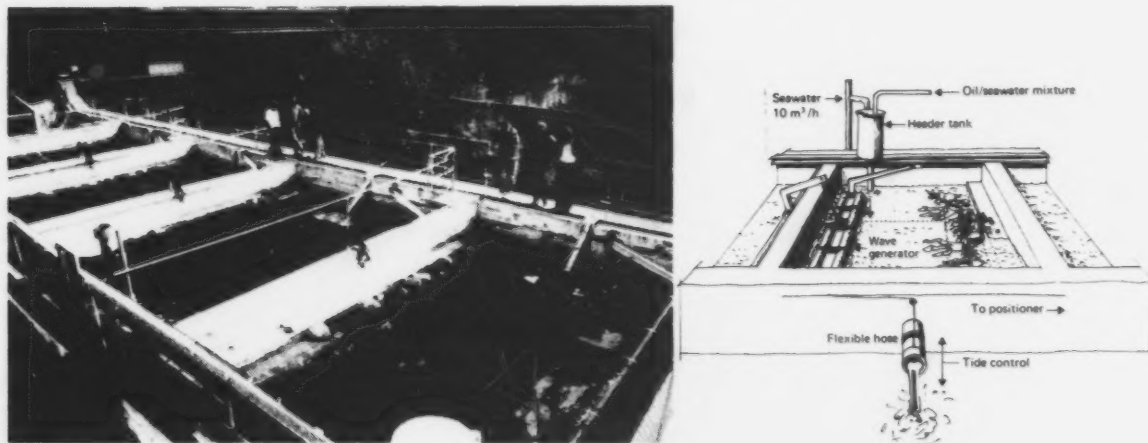


Figure 1. Left: photograph of the four rocky shore mesocosms. Right: sketch of one of the basins with technical installations.

level in a 12 hours sinusoidal cycle following the tidal rhythm and with nominal amplitude 30 cm.

In October 1979 rocks with algae and animals from the littoral zone were transplanted to the basins and positioned on the tribunates at the same tide level as on the shore. Then the basins were left undisturbed for 3 years for community development and further recruitment by self propagation and settlement of spores and larvae brought in with the water. At the end of this period about 50 species of algae and animals were established in the basins (Bokn and Moy 1985) giving four communities typical of sheltered shores in the middle and outer Oslofjord region.

Oil experiment

From 15 September 1982 to 27 September 1984 two of the communities were continuously exposed to a water accommodated fraction (WAF) of diesel oil in sea water, while the other two communities were run as controls. The WAF was produced by continuous mixing of sea water (preconditioned to 12.5°C) and pure diesel oil in volume proportion 1800:1 in a 580 liter mixing/separation system (Figure 2). After removal of excess oil by continuous surface skimming, the WAF was pumped into the main water inlet to the test basins at nominal dilutions 75:1 and 300:1 for the high oil basin (HO) and low oil basin (LO) respectively.

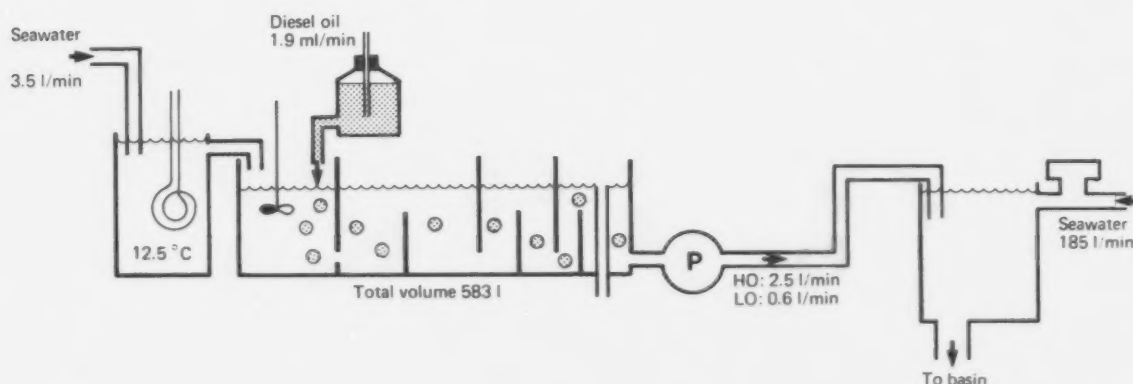


Figure 2. Diagram of the WAF production and dosing equipment.

ANALYTICAL PROGRAMME

Basin conditions

The water temperature of the four basins as well as at 1m depth in the fjord was monitored by permanently installed probes connected to potentiometric recorders. Salinity was recorded continuously in one of the control basins by a conductivity probe. In addition salinoterm readings of temperature and salinity were taken daily or several times a week. From January 1984 to December 1985 the particle concentration and size distribution were analysed once a week from the HO and one control basin.

Oil analysis

The hydrocarbon concentration of the WAF was monitored routinely 3 times a week throughout the 25 months by spectrofluorometric analysis of samples taken at the outlet from the mixing/separation unit (Figure 2) and at the inlet to the basin header tanks. Duplicate 50 ml WAF samples were extracted with n-hexane, fluorescence intensity of the extracts measured at excitation 265 nm and emission 322 nm, and the intensity converted to corresponding diesel oil units. The concentration of hydrocarbons in the basin water (1 liter samples) was monitored once a week during the last year of exposure by the same analytical procedure. The relation between WAF and basin concentrations the last year was used to calculate basin concentrations during the first year from the WAF concentrations. A small set of WAF and water samples have also been analysed by GC and GC/MS after extraction with dichloromethane.

Biological investigations

The component studies performed during the exposure and recovery periods were:

- Gross community structure and population size of macroscopic algae and animals.
- Colonization pattern, growth, and the effect of grazing on the initial sessile communities.
- Metabolism of the first generation rock cover community.
- Individual growth of knotted wrack (Ascophyllum nodosum), kelp (Laminaria digitata), green algae (Ulva lactuca), and periwinkles (Littorina littorea).
- Population dynamics and population genetics of mussels (Mytilus edulis), periwinkles, and barnacles (Balanus spp.).
- Energy conversion and utilization, biochemical, cytochemical and histological stress responses in mussels and periwinkles.
- Tissue levels of hydrocarbons in important species.

RESULTS

Environmental regime

The mean annual basin temperature for the period 1980 to 1985 was 9.50°C. The mean monthly temperature ranged from 18.87°C in August to 0.55°C in March, compared to 18.27°C and 0.42°C in the fjord. During the two years of oil exposure the mean temperatures in these months were slightly higher: 19.44°C and 1.21°C respectively. The mean annual salinity in the fjord as well as in the basins from 1980 to 1985 was 25.10 ppt (parts per thousand), and monthly mean range was from 30.49 ppt in January to 17.79 ppt in June. Hence, the basin communities experienced the same large annual environmental range as in the Oslofjord.

Oil exposure

The overall mean basin concentration of hydrocarbons during the exposure period was 129.4 µg/l (diesel oil equivalents) and 30.1 µg/l for the H0 and L0 basins respectively, when the background level of 5.6 µg/l was subtracted (Table 1). This shows the concentration in the H0 basin to be 4.3 times that of the L0 basin. The concentrations were slightly higher and fluctuated more during the initial period in 1982 than for the rest of the period. The GC analysis gave lower estimated means than the corresponding fluorescence values: 82.3 and 22.7 µg/l in H0 and L0 respectively. The GC analysis further demonstrated a relative enrichment in aromatic hydrocarbons in the H0 basin to 58 % of the total extractable oil compared to 23 % in the original diesel oil (Bakke and Sørensen

1985). Since both analytical procedures used the same diesel oil as reference, this enrichment explains why fluorescence analysis (responding to the aromatics only) gave higher estimates of mean basin concentrations than the GC analysis.

Table 1. Hydrocarbon concentration in basin waters in $\mu\text{g/liter}$ (mean $\pm$ s.d) from fluorescence and GC analyses.

	Basin analysis Aug83-Sept84	Estimated means from WAF concentration				GC GC analysis
		1982	1983	1984	1982-84	
HO basin	127.3 $\pm$ 49.5	154.9 $\pm$ 50.0	123.1 $\pm$ 27.5	127.7 $\pm$ 28.3	129.4 $\pm$ 33.3	82.3 $\pm$ 64.4
LO basin	27.9 $\pm$ 11.6	42.4 $\pm$ 15.9	28.8 $\pm$ 7.8	27.4 $\pm$ 7.2	30.1 $\pm$ 10.3	22.7 $\pm$ 25.5
HO/LO	4.6	3.7	4.3	4.7	4.3	3.6

Tissue levels of hydrocarbons

Sporstøl & al. (in prep.) detected significant accumulation of aromatic hydrocarbons in Mytilus edulis and Littorina littorea. Maximum magnification above average background was 21 times for M. edulis and 12 times for L. littorea from HO. The algae Ascophyllum nodosum and Fucus serratus were also found to accumulate hydrocarbons to maximum 15 and 8 times above background respectively, but the absolute tissue concentration in the algae was less than one third of that in the animals. A. nodosum and especially M. edulis exhibited a gradual increase in tissue hydrocarbons with time. L. littorea lost 75 % of the aromatics during summer, possibly in connection to spawning. F. serratus showed no significant variation with time.

The LO tissue levels were consistently lower than the corresponding HO values. The mean HO/LO ratio in net tissue aromatic hydrocarbons (control levels subtracted) of A. nodosum: 4.1, F. serratus: 3.9, and L. littorea: 3.6 corresponded well to the HO/LO ratio in water levels of hydrocarbons (Table 1), whereas a ratio of 1.3 in M. edulis indicated that accumulation was less dependent on dose in the mussels.

M. edulis and L. littorea selectively accumulated more of the heavier fraction of the diesel oil, whereas the chromatograms from the algal tissues resembled that of the water extracts (Sporstøl & al. in prep.). Together with the lower and more constant tissue burden in the algae this indicated that the aromatics were adsorbed to the mucoid surface of the algae rather than being taken up by the tissues.

Biological effects

Bokn and Moy (1985) showed that most of the populations changed in density with time, either a general decrease (e.g., Fucus distichus and Asterias rubens), an increase (e.g., Phymatolithon lenormandii and Chondrus crispus), or as function of season (e.g., F. serratus, Laminaria digitata, L. littorea, and Balanus spp.). Growth of the two green algae Cladophora rupestris and Ulva lactuca seemed to be stimulated by the oil exposure, whereas M. edulis gradually disappeared from the oil basins. The population of small motile crustaceans

(amphipods and isopods) living among the macroalgae seemed also to disappear from the oil basins (Bakke unpublished). Cluster analysis of the community structure (Bokn and Moy 1985) indicated a gradual shift from 4 communities with minor differences at start of the exposure to clearly separated exposed and control communities in the end.

Investigation of the primary community development on bare rock was done by use of 10x10 cm granite settling tiles. Half of the tiles in each basin were supported freely in the water, and hence protected from winkle grazing. Bokn (1984) and Follum (1985) reported that community establishment on the protected tiles in the H0 basin was characterized by strong growth of diatoms in contrast to the other basins where chloro- and phaeophyceae were common, but total biomass was not different (Bokn 1984). Primary growth on the grazed tiles was generally less dense and the similarity in species composition among the basins greater than on the protected tiles. The differences encountered were attributed to different grazing intensity rather than the oil. Pedersen (1985) showed that net and gross primary production and light efficiency was subnormal in the protected tile communities of H0 during summer, and respiration was enhanced, in comparison to the adjacent control basin. The results demonstrated that primary community development was affected quantitatively and metabolically by the oil, but also that the effect of grazing was even greater and could mask this almost completely.

Although the dominant brown algae seemed unaffected with respect to population size, the individual growth was negatively affected. Tagged individuals of A. nodosum and L. digitata showed significantly subnormal length increment during the second year of oil exposure both in the H0 and L0 basins, but not during the first year (Bokn 1985). The delay in response inferred that growth was reduced only when the initial growth zone, the meristem, had been exposed to oil prior to the onset of a new growth season. Individuals of U. lactuca showed the opposite response: a significant stimulation of growth in the presence of oil in both oil basins from June to August 1984 (Bakke unpublished).

The most severe population decline during exposure was shown by M. edulis. Bokn and Moy (1985) recorded 100 % mortality within 15 months in the H0 basin and within 20 months in the L0 basin. Mortality was negatively correlated to size. Thome and Walday (1984) found in the H0 basin that 50 % mortality was reached within 2 months in the size class 10-15 mm shell length, whereas more than 5 months exposure was required to cause 50 % mortality in the 20-25 mm size class.

The cause of mussel death was directly and indirectly lack of ability to obtain sufficient energy for growth and maintenance. Widdows (1984) detected severely reduced feeding rates and absorption efficiency in both H0 and L0 mussels, resulting in significantly lowered scope-for-growth (SFG) compared to control individuals. The reduction in absorption efficiency was not dose related. The energy deficiency was also reflected in enhanced ammonia excretion suggesting excessive use of protein storage material (Widdows 1984), and in reduced volume of nutrient storage cells (Lowe and Pipe 1985). Strongly reduced growth rate in most size classes of the H0 population was also reported by Thome and Walday (1984) during the first year of exposure. Lowe and Pipe (1985) observed enhanced frequency of atresic (partly resorbed) gamete cells in the exposed mussels, most severely in H0, and suggested a direct cytotoxic effect of the oil on the gametes linked to an observed destabilization of lysosomes (Moore 1984).

Another effect of the exposure, and possibly linked to the energetics, was reduced ability by the mussels to produce byssus threads. Such response to oil has also been observed in other experiments (Lindén 1977, Bakke unpublished). This caused the mussels to drop to the bottom of the basins where they were more

easily subjected to predation by crabs (Carcinus maenas) and starfish (Asterias rubens). The nutrient state of the mussels also weakened the shell adductor muscle (Moore pers. comm.) which further increased their vulnerability to predation. Yet, predation was not the only cause for mussel mortality, as this was also observed in caged individuals (Thome and Walday 1984, Lowe and Pipe 1985). Lowe and Pipe (1985) also showed that timing of the oil exposure relative to the nutrient storage cycle had strong influence on survival. Mussels transplanted to HO in June, i.e., during or just after spawning, experienced 71 % mortality after 80 days, whereas mussels transplanted in January, when nutrient reserves were high, showed only 27 % mortality after 227 days in the HO basin.

Widdows & al. (1985) observed faster recovery and an initial "overshoot" in feeding rate in the HO mussels after transfer to clean water. On basis of this and the fact that the tissue hydrocarbon levels and the effects of oil on physiology and cell chemistry of the mussels did not exhibit a clear dose related response, Widdows (1984) suggested that the high mortality might have selected a more resistant phenotype in HO. On the other hand, electrophoretic analysis of enzyme polymorphism both in M. edulis, L. littorea and Balanus balanoides gave little evidence to state that the exposure had caused short term genetic selection in any of these species (Fevolden and Garner 1986, Fevolden and Sigurdsson 1985). The lack of dose dependence in some of the physiological and cytological responses could be due to the nutrient reserves functioning as a buffer against environmental change during periods of gamete production as was postulated by Bayne (1975).

In L. littorea, the most important grazer in these communities, the overall mortality was small. Even before the oil exposure started there was a considerable difference in population size among the basins with highest and lowest density in the two control basins (Bokn and Moy 1985, Lystad and Moe 1985). This difference was persistent throughout 1982-1985. Bokn and Moy (1985) reported a general decrease in winkle density on the basin tribunes from July 1982 to August 1984, significant in the HO basin and the control basin having highest density. Lystad and Moe (1985) reported significantly higher mortality in HO than in the other basins on basis of mark-and-recapture estimates of total basin densities during the first year of exposure. HO and LO were also the only basins where dead adult shells were recovered to any extent (ibid.).

Mortality of the early L. littorea juveniles was clearly enhanced in HO and LO although the input of egg capsules was the same in all basins (Lystad and Moe 1985). Generally HO had the smallest population of individuals less than 6 mm in shell height, followed by LO which again had less than the control basins. Occurrence and size frequency of dead winkle shells on the bottom of the basins gave further evidence to the impression of enhanced juvenile mortality caused by the oil (ibid.).

Effect of oil on individual growth of L. littorea was obscured by high variability within the populations. Mean growth rate in the exposed basins was within the range found in the control basins. This range was large and suggested that growth was negatively dependent on density (Lystad and Moe 1985). Growth rate in both HO and LO was, however, clearly lower than in the control population which demographically was most similar to the exposed populations.

In spite of the lower mortality and less clear effects of oil on growth, the physiological and biochemical responses in L. littorea were similar to those registered in M. edulis. Feeding rates of HO and LO winkles on a diet of U. lactuca were significantly less than the control rates (Widdows 1984, Bakke 1985b). Food absorption efficiency was clearly less than in the controls throughout the summer 1984 (Bakke 1985a), but not in May-June the year before (Widdows 1984). Subnormal absorption ability was also inferred from signs of disorganization in

the digestive gland tissues and significant lysosome destabilization in the digestive cells (Moore & al. 1985). The control populations showed a wide range in scope-for-growth, but the HO and LO individuals had consistently lower mean SFG than these. The difference in SFG between HO and LO winkles was not systematic and not related to dose (Bakke 1985a).

Recovery after oil exposure

Analysis of the basin water after the exposure was terminated showed significant release of hydrocarbons from organisms, rock surfaces and sediments only during the first day. One week after the WAF input had been stopped, no elevation in fluorescence intensity was detected in HO even after 6 hours without water exchange and with the wave generator on (Sørensen unpublished).

Since the oil exposure was terminated at the end of the reproductive season an immediate recovery in density of affected populations was not expected. Yet, the first new M. edulis recruits were recorded in the HO basin in less than one month (Bokn pers.comm.). A similar recruitment to the LO basin was not observed. The transect registration of community structure continued during the 12 months recovery phase, but no data have yet been presented. However, trap samples of amphipods and isopods taken after 10 months recovery showed that densities in both HO and LO were within control range (Bakke unpublished).

Recovery in physiology and cell responses of M. edulis was studied through transplants from exposed to clean basins. Widdows & al. (1985) registered a partial recovery in physiological responses of both HO and LO populations within 10 days during May 1983 and 1984. After 22 days the HO individuals had higher feeding rates and SFG than the controls resulting in catch-up growth. The LO mussels showed slower recovery and no such overshoot in feeding. After 55 days both populations were within control range. In May-June 1984 Lowe and Pipe (in press) recorded significant increase in volume of mantle storage cells and reduction in frequency of atretic gametes within 55 days depuration. At the same time Moore & al. (1985) recorded full recovery of digestive cell lysosome stability, although no sign of recovery was detected during the first 20 days. Hence, most effects of the oil on individual M. edulis had vanished within about 2 months.

The HO population of L. littorea exhibited a similar temporary overshoot in feeding rate as M. edulis two weeks after the oil exposure had been terminated (Bakke 1985b). No recovery was recorded in the LO individuals at that time, and measurements performed after 7 and 11 months still showed subnormal feeding rates in the LO winkles. After 11 months L. littorea from both HO and LO had still not depurated all the aromatic hydrocarbons on the tissues (Sporstøl pers.comm.). These results indicate slower recovery than in the mussels, at least in the LO winkles. Yet, absorption efficiency had returned to control range within 2 weeks (Bakke 1985b), and Moore & al. (1985) showed complete recovery of lysosome stability within 4 days. Digestive tissue organization was partially restored within one week (ibid.).

DISCUSSION

The hydrographical conditions in the mesocosms reflected the extreme seasonal variation which is a characteristic feature of the Oslofjord region. The summer surface temperature is frequently above 20°C; in winter it is normally below zero. (This has even been recorded at 40 m depth outside Solbergstrand.) The shallow water flora and fauna are typically boreal. Hence, the findings in this experiment should have relevance to chronic oil inputs also in the arctic

region.

The mean hydrocarbon level of 129.4 $\mu\text{g/l}$ in the water of the HO basin was similar to levels applied in earlier mesocosm experiments with other types of communities, such as at M.E.R.L., Narragansett Bay (90-190 $\mu\text{g/l}$, Oviatt & al. 1982) and Loch Ewe, Scotland (100 $\mu\text{g/l}$, Davies & al. 1980) where significant effects on populations were reported. The level was chosen on basis of these experiments to give an exposure where the chances of producing effects were great. The LO exposure of 30.1 $\mu\text{g/l}$ was within ranges recorded by fluorescence in polluted estuary and harbour areas, as well as around North Sea oil rigs (e.g., Michalik and Gordon 1971, Marchand and Caprais 1985, Massie & al. 1985). It is at the bottom end of the range in concentrations where significant effects have been detected before.

Although the difference in appearance between HO and the other basins was clear, especially during the summer of 1983 and 1984 when mats of green algae covered HO, the results have demonstrated few negative effects on gross population sizes. The severe mortality in M. edulis was unexpected since mussels frequently occur in heavily polluted regions. One possible explanation is the constancy of oil particles in the water giving the mussels no leeway to compensate for the energy loss through shorter periods of excessive feeding. The effects were less dramatic in other species, but were reflected in growth, physiology, tissue organization and cell chemistry of the species investigated.

The results demonstrated long term biological effects and clear deterioration even at about 30 $\mu\text{g/l}$ and, furthermore, that no simple relation existed between exposure grade, severity of effects and recovery rate. The frequent lack of dose dependence could be due to several factors. The long duration of the exposure even to as low as 30 $\mu\text{g/l}$ may have exceeded compensation limits for certain processes. In some organisms the HO exposure may have caused better phenotypic adaptation to the stress than in LO, as could be inferred from the faster physiological recovery in M. edulis and L. littorea from HO. Lack of difference between HO and LO could also have been result of buffering processes in the community (e.g., competition, predation) and in the individual (e.g., behaviour, nutrient administration, detoxification). Some of these ideas are assumed to be elucidated in the final papers from the experiment. Still, the results left no doubt that exposure to about 130 $\mu\text{g/l}$ of oil caused stronger overall deterioration than exposure to 30 $\mu\text{g/l}$.

The results reported hitherto give little basis to suggest irreversible effects of two years chronic oil exposure, as full recovery from most effects seemed to have occurred within one year. The indication of slower recovery in L. littorea than in M. edulis could be tied to the difference in food source of the two species. With the high water turnover in the basins the mussels would have clean food almost immediately after the dosing ended, i.e., the same situation as when the mussels were transplanted to a control basin, whereas the reduction in oil input to L. littorea was dependent on the depuration rate of the substrates. The rapid recovery of cell functions reported by Moore & al. (1985) occurred in winkles transplanted to a control basin with clean food, whereas the slow recovery in feeding rate and depuration was shown by winkles still in the HO and LO basins. Analysis of potential winkle food scraped off the HO walls during exposure showed 6 times magnification in aromatics above control levels (Sporstøl pers. comm.). Although corresponding data from the recovery phase are not yet available, this suggests that the winkles had to feed on contaminated substrates for a while after the water exposure ended.

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PHYSIOLOGICAL EFFECTS OF OIL AND OF CHEMICAL TREATMENT OF OIL
ON EGGS OF PLAICE, PLEURONECTES PLATESSA

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INTRODUCTION

Because of the inadequacy of mechanical methods for treatment of oil spill (Benterud et al., 1985), it is in some cases relevant to use chemical methods. The development of new, presumably less toxic products has led to increased international interest in dispersants as a means of combating oil pollution.

To know the environmental consequences of the use of different chemicals, it has, in addition to testing effectivity as dispersants, been desirable to look at the toxic effects of both oils and dispersants on marine organisms. Many investigators have studied the effects of oil on fish eggs and larvae because these stages are fragile and sensitive to natural environmental stress. Developmental abnormalities have been demonstrated in embryos exposed to oil and oil components (Lønning, 1977, Linden, 1978 and Kühnhold, 1974). Furthermore Linden found reduced growth in fish larvae as a response to oil exposure. However knowledge about physiological effects of oils and dispersants is very scarce.

The purpose of the present study has been to investigate the eggs and early larvae of Plaice, Pleuronectes platessa. It has been the intension of this investigation to contribute to a descision making model, intended to be utilized in the contingency planning of alternative clean-up operations.

MATERIAL AND METHODS

Experimental Fish Eggs

Parent fishes were collected in the Borgenfjord, Norway (63° 26' N, 10° 24' E) in January 1985 and 86 and held nearby at The Biological Field Station at

Mosvik. Eggs were artificially fertilized and incubated in laboratory at 5.0 °C. The eggs were exposed to different oils from the time they reached the stadium of the first heart beat (Apstein, 1909).

Mortality

Groups of about 300 eggs were exposed to 100 ml of different dilutions of various stock solutions. The eggs were held in complete darkness during the exposure and the mortality was measured each day during a period of eight days. The mortality percentage could then be calculated (Lloyd, 1979).

Flotation

Flotation was registered by taking water samples with a syringe and measuring the salinity at the flotation level of the eggs when placed in a plexiglass-column with an established salt gradient.

Perivitelline Space (PVS)

The volume of the perivitelline space was determined from the fructose space of the egg (Riis-Vestergaard, 1981). Fructose at a known concentration diffused into the perivitelline space and was then washed out from a known number of eggs into a known amount of fructose-free water. The concentration of fructose was determined with a Bausch & Lomb Spectronic mini 20 spectrophotometer after the method of Kulka (1956).

Concentrations of free amino acids (FAA)

Eggs were dried carefully by rolling them for a moment over filterpaper and then shock-freeze them three times in liquid nitrogen to burst the embryonic cells. They were then centrifuged at 10 000 rpm for 20 minutes in a MSE high speed 18 cooling centrifuge at 5 °C. 25 ul of the supernatant was diluted with 100 ul distilled water, and the proteins were removed by adding 50 ul 20% sulfosalicylic acid and centrifuged. 50 ul of the supernatant was mixed with 30 ul distilled water and 20 ul OPA-reagents and injected into a Varian Vista 5500 HPLC after 10 minutes.

Experimental procedure

At the stage of the first heart beat the eggs were transferred to the water soluble fraction (WSF) of Statfjord A+B crude and topped (150 °C) oil, emulsion (50:50% sea water in oil topped at 240 °C) and diesel oil. These solutions were made according to the Trondheim method (Østgaard & Jensen, 1983), and all exposures of egg were done in undiluted stock solutions. Analysis of the WSF's has not yet been done, but regarding the crude oil water solution, the total concentration of oil components is expected to be around 17 ppm

(Østgaard & Jensen, 1983). About 6 ml of eggs was exposed to one liter of test solution in a 3 l Erlenmeyer bottle for 96 hours at complete darkness and at 5 °C.

RESULTS

Mortality

The mortality results (Fig.1) show that the water soluble fraction (WSF) of crude oil was the more toxic of the solutions. None of the concentrations of WSF for topped oil, oil emulsion or diesel oil were as high during 8 days as to reach the LC-50 level. It was, however, observed an increased mortality in the highest concentrations of WSF of the topped oil. These mortality results imply that undiluted stock solutions should be used in the sublethal studies.

Flotation

The ability to flotata was significant lowered after exposure to the WSF's of crude oil and oil emulsion (Fig.2). However, eggs exposed to diesel oil had neutral buoyance at a lower salinity than the control.

Volum of perivitelline space and relative water content of the egg

The volume of the space between chorion and the embryo, the perivitelline space (PVS), did not change significantly after exposure to WSF of crude oil (Fig.3). However, the exposure to diesel gave about 1/3 relative increase in the PVS and represented 5% more of the total egg volume.

The relative water content of embryo and yolk mass did, on the other hand, not change during the same exposures (Tab.1).

Concentration of free amino acids (FAA)

The concentrations of many of the free amino acids in the egg increased after exposure to the WSF's of crude and diesel oil (Tab.2). This increase was especially conspicuous for serine, alanine, valine, isoleucine, leucine and lysine. In addition, the amino acids aspartic acid and asparagine showed up in the exposed eggs. Put together the total concentration of amino acids nearly doubled during the 96 hour exposures.

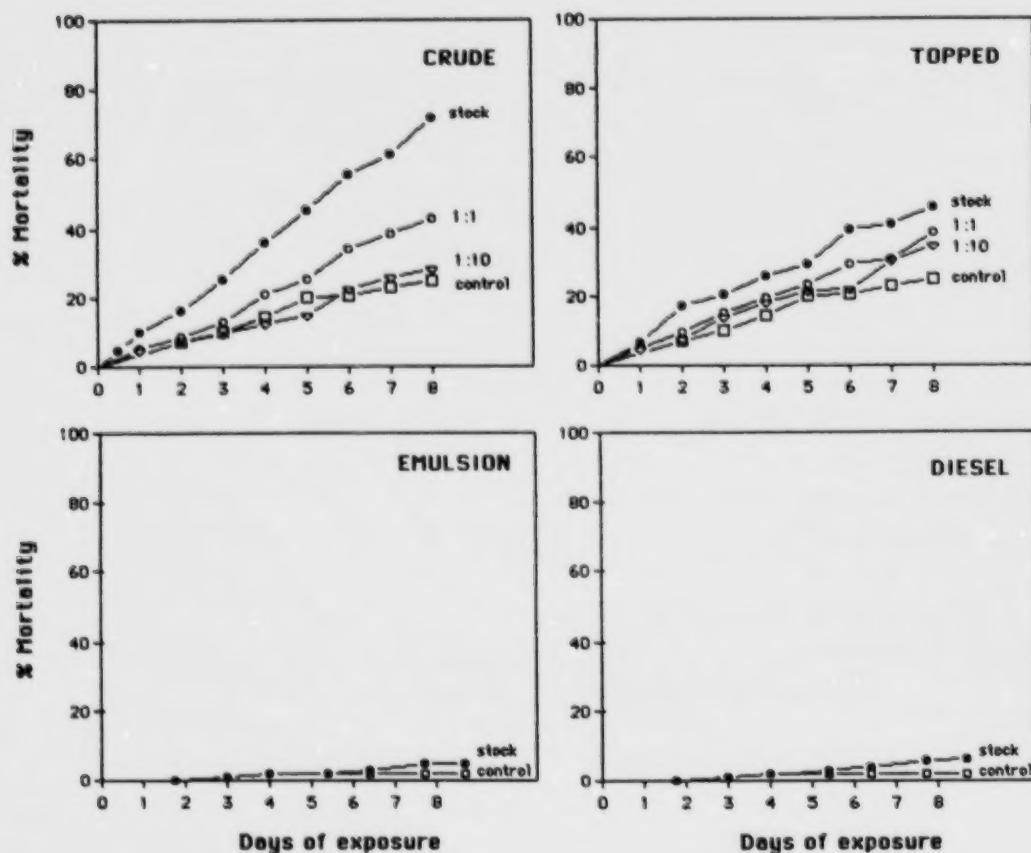


Figure 1. Mortality/Time curves for eggs of Plaice, *Pleuronectes platessa* exposed to pure sea water and 1, 1:1, 1:2, 1:5, 1:10 and 1:100 of the stock solution of Statfjord A+B crude oil, topped crude oil (150 °C), 50:50 water in oil emulsion (oil topped at 240 °C) and diesel oil. All the stock solutions referred to are made according to the Trondheim method. Eggs were held at 5.0 °C and in total darkness.

Control	Crude Statfjord A+B oil (stock)	Diesel oil (stock)
90,63 ±0,10% (3)	90,88 ±0,12% (3)	90,40 ±0,09% (3)

Table 1. Relative water content of embryo and yolk mass of Plaice, *Pleuronectes platessa* after exposure to the WSF's of Statfjord A+B crude oil and diesel oil. Exposure time was 96 hours at 5.0 °C and total darkness. The WSF's were made by the Trondheim method.

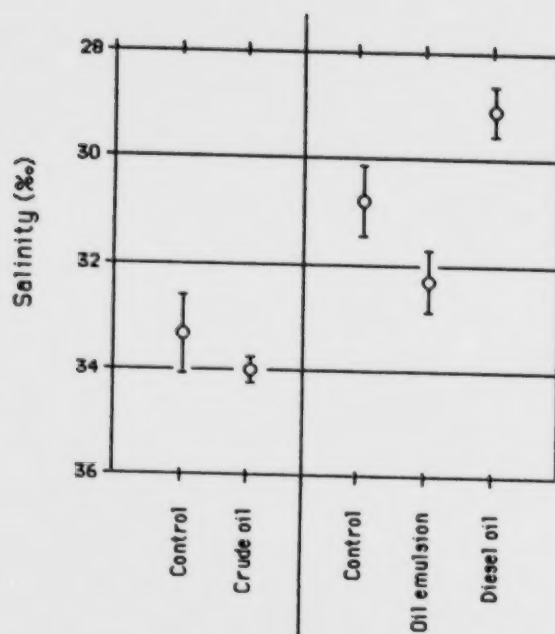


Figure 2. Flotation of eggs of Plaice, *Pleuronectes platessa* as function of water salinity at neutral buoyance. The eggs were exposed to the WSF of Statfjord A+B crude oil in one test serie and to the WSF's of 50:50 water in oil emulsion (topped at 240 °C) and diesel oil in another test series. Values are mean $\pm$ SD and number of eggs is 8 for each exposure. Exposure time was 96 hours at 5.0 °C and total darkness. The WSF's were made by the Trondheim method.

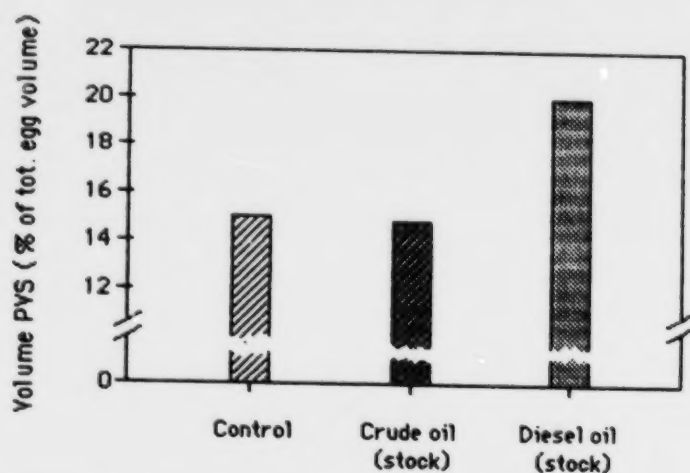


Figure 3. Volume changes in the perivitelline space of eggs of Plaice, *Pleuronectes platessa* after exposure to the WSF's of Statfjord A+B crude oil and diesel oil. Exposure time was 96 hours at 5.0 °C and total darkness. The WSF's were made by the Trondheim method. Each bar represents the mean value of four groups of 20 eggs. Maximal SD was 5%.

Table 2. Changes in the concentrations of free amino acids ($\mu\text{mol/kg}$ tissue water) in tissue homogenate of eggs of Plaice, *Pleuronectes platessa* after exposure to the WSF of diesel and crude Statfjord A+B oil. Exposure time was 96 hours at 5.0 °C and total darkness. The WSF's were made by the Trondheim method. About 200 eggs were homogenated in each group. The concentrations are adjusted in regard to the volume of the perivitelline space.

Amino acid	Control	Crude Statfjord A+B oil (stock)	Diesel oil (stock)
Aspartic acid	2	128	78
Glutamic acid	476	573	394
Asparagine	2	374	346
Serine	400	1.533	1.272
Glutamine	346	520	487
Histidine	254	352	318
Glycine	548	843	857
Threonine	316	416	400
Arginine	1.687	2.820	3.022
Tyrosine	364	421	432
Methionine	311	386	437
Valine	970	1.601	1.690
Phenylalanine	331	411	440
Isoleucine	837	1.510	1.596
Leucine	1.131	2.073	2.132
Lysine	1.031	2.690	2.467
Sum FAA	9.430	17.213	16.889

DISCUSSION

The low effect of the WSF's of diesel and emulsion on mortality is likely to be due to the low amount of highly volatile components in these oil types. It is well

known that highly volatile hydrocarbons tend to go into the water phase. In connection with important spawning areas it therefore seems more reasonable, in terms of reducing the effects of an oil spill with the use of dispersants, to focus on crude and topped oil spills. Preliminary experiments with fish eggs indicate that there are great differences between dispersants with respect to toxicity. These differences have to be investigated thoroughly before the dispersant to be used is chosen.

The perivitelline membrane of Plaice eggs and most other fish eggs are characterized by a very low water permeability (Potts & Eddy 1973). This phenomenon is expected to be an adaptation to the lack of active transport mechanisms in early embryos. Grasdalen & Jørgensen (1986) showed that exposure to WSF's of Statfjord A+B crude oil doubled the water permeability. At a stage when few transport mechanisms are activated, it could be assumed that this effect is due to an increased passive membrane leakage. The relative water content of the eggs was found to be unchanged (Tab.1) indicating that the water content is regulated by a mechanism which is not understood. The increase in the concentration in the eggs of several free amino acids found after crude oil exposure may indicate that these solutes are involved in the water balance of stressed eggs.

The Plaice eggs are pelagic, but contain few if any oil droplets. However, the bulk of the dry weight is made up by proteins, which are less dense than the ions. The lower salt content of the egg reduces the overall density to a value slightly less than that of sea water (Potts & Eddy 1973). The lower ability to keep neutral buoyance after exposure to crude oil and oil emulsion (Fig.2) may be due to salts penetrating the normally nearly impermeable perivitelline membrane. This may cause the density of the egg to increase. The opposite effect, i.e. decreasing egg density, which is found in eggs exposed to diesel oil, is more difficult to explain. It may be connected with the increased volume of the perivitelline space found in diesel exposed eggs (Fig.3).

The amino acids aspartic acid and asparagine, which occur only after oil exposure, may indicate an effect on the amino acid metabolism or on the amino acid transport mechanisms. Similar effects have been found more pronounced in connection with exposure of eggs to the WSF's of combinations of crude oil and dispersants.

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ALASKA CLEAN SEAS TEST AND EVALUATION OF FIRE CONTAINMENT BOOM

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ABSTRACT

Four fire containment booms have been tested and evaluated for their resistance to fire during 24-hr exposures to burning crude oil. Seven individual burn tests were conducted using FireGard Boom (Kepner Plastics Fabricators, Inc.), PYROBOOM (Globe International, Inc.), SWEPI Fire Containment Boom (Shell Western E&P Inc.), and 3M Fire Boom Blanket (3M/Ceramic Materials Department). Each boom was connected in a closed loop and placed within a steel tank 3 m (10 ft) on a side. Thermocouples were positioned within the booms and at various locations in the test tank. Cook Inlet crude oil was fed continuously to the center of each containment area at approximately 2.8 to 3.8 liters/min (3/4 to 1 gal/min) and ignited. The performance of each boom was documented on videotape, and temperature profiles were recorded for each thermocouple. The results of these tests are summarized along with an overall assessment of each system's physical and operational strengths and weaknesses. Included is a summary of several tests conducted to evaluate the oil-holding capacity and wave-riding characteristics of each boom. These tests were conducted with and without an oil simulant in waves up to 0.6 m (2 ft) in height and with currents of 0.2 to 0.6 m/sec (0.4 to 1.2 kt).

INTRODUCTION

This paper contains a summary of a much more extensive report prepared by Spiltec for Alaska Clean Seas (ACS), an oil-industry-sponsored oil spill response organization based in Anchorage, Alaska. The original report, Test and Evaluation of Fire Containment Boom (Spiltec, 1986), presents the results of one of several R&D efforts sponsored by ACS during 1985. Shell Western E&P Inc. (SWEPI) served as the ACS administrator during all phases of the project.

Four fire containment concepts were evaluated during the course of this project including:

- o FireGard Boom -- A bottom-tensioned, reelable boom, manufactured by Kepner Plastics Fabricators, Inc., with two layers of fire-resistant fabric positioned over a coil and foam flotation system.

- o PYROBOOM -- A fence boom manufactured by Globe International, Inc. and using external steel hemispherical floats. The above-water portion of the boom is protected by a wire-reinforced, specially coated refractory material, while the skirt of the boom is a conventional impermeable material weighted with lead discs.
- o SWEPI Fire Containment Boom -- A bottom-tensioned, cylindrical-flotation boom, designed by Shell Western E&P Inc. (SWEPI), and manufactured by Fire Control, Inc., with multiple layers of fire-resistant, wicking fabric positioned over steel canisters for flotation. An additional sacrificial layer and a coarse wire-mesh barrier are used externally for abrasion resistance.
- o 3M Fire Boom Blanket -- A multi-layered, fire-resistant blanket, provided by 3M/Ceramic Materials Department, for use as an add-on with most conventional types of boom for the containment of burning oil. The blanket is held in position by any number of fastening systems requiring installation of the fasteners to the support boom in advance.

Other existing fire-resistant booms were not included in this test program because they did not meet certain operational and financial constraints.

OBJECTIVES

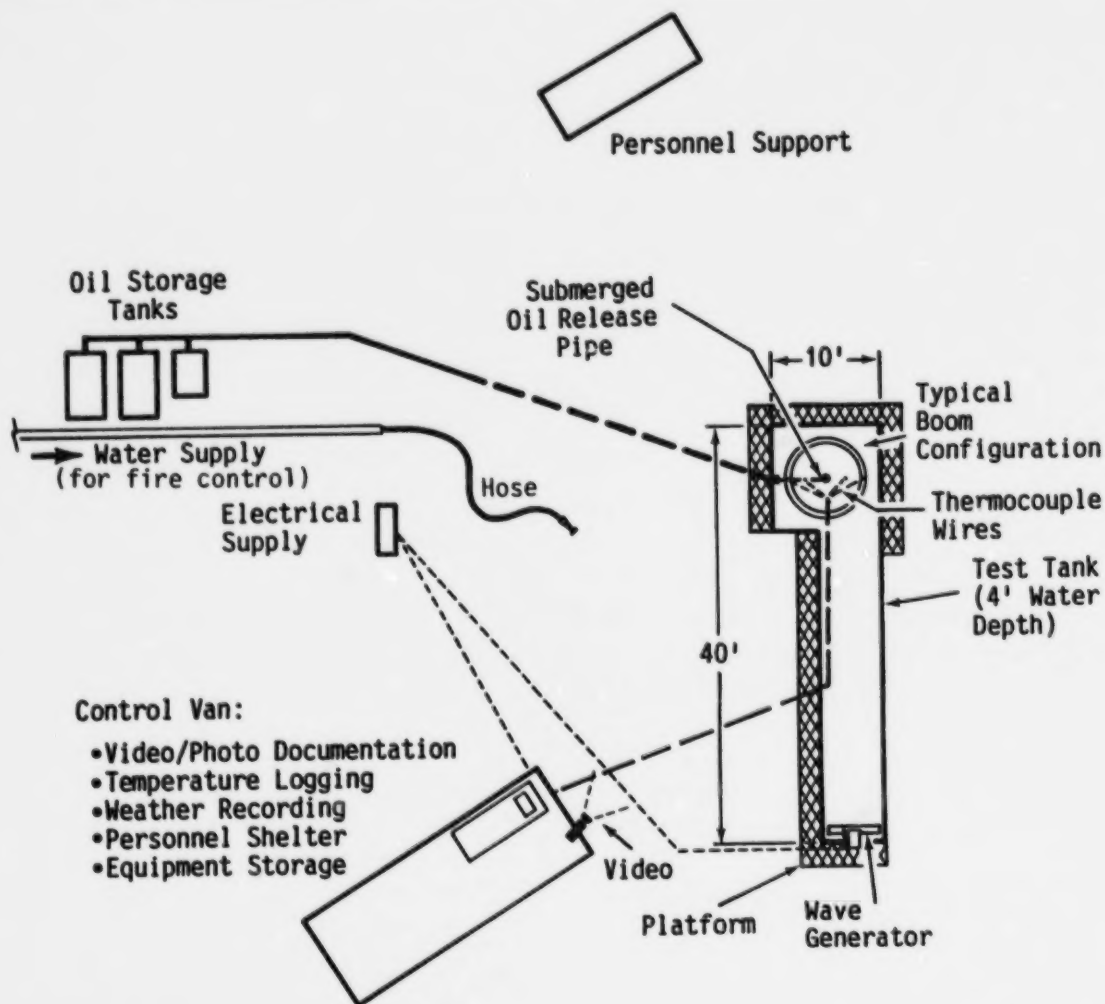
Several individual burn tests were conducted in a test tank at an onshore facility in Kenai, Alaska. The objective of these tests was to expose the above fire containment systems to burning crude oil for 24 hr. The survivability of each system was to be evaluated during each burn test; and qualitative assessments were to be made of such characteristics as flexibility, strength, weight, and ease of handling.

During separate wave-tank tests at Shell Oil Company's Westhollow Research Center in Houston, Texas, each of the above containment systems would then be exposed to a range of towing speeds and wave conditions. These tests (funded independently by SWEPI) would serve to evaluate the oil or oil-simulant holding characteristics and the wave-riding and tow-stability aspects of each system.

TEST FACILITIES AND PROCEDURES

Kenai Test Facilities

The test facilities for the fire containment boom burns were set up at the Kenai Community College's fire control training site in Kenai, Alaska (Figure 1). All tests carried out during this project were conducted with Cook Inlet crude oil (35° API) provided by SWEPI. All tests were also conducted in fresh water. Prior to each test, thermocouples were mounted on posts in the test tank so that each thermocouple could be positioned a few inches above the water surface at several locations within the burn region of each boom. In addition, project personnel worked with the manufacturer's representatives prior to each burn test to determine the desired locations for thermocouples on or within the boom to be tested.



Fire Containment Boom Test Facility

Location: Kenai Community College Fire Control Training Site, Kenai, Alaska

Test Tank: 40-ft long, 5-ft-high steel tank with 10 ft x 10 ft area for placement of boom.

Oil Storage & Transfer: Two 500-gal containers plus one 300-gal container, elevated to provide 3/4 to 1 gal/min continuous gravity feed to test tank.

Oil: Fresh Cook Inlet crude oil (35° API)

Support Facilities & Equipment: As shown above.

FIGURE 1 KENAI TEST FACILITY

Approximately $7\frac{1}{2}$ m (25 ft) of boom was requested from each manufacturer to provide a closed circle of boom nearly $2\frac{1}{2}$ m (8 ft) in diameter. At the center of each burn region, a vertical pipe was positioned so that crude oil could be released approximately 30 to 40 cm (1 to 1.3 ft) below the surface of the water. A thermocouple was positioned on the oil discharge pipe to record water temperatures approximately 50 cm (1.6 ft) below the fire during each burn test. The gravity flow of oil was adjusted to provide from 2.8 to 3.8 liters/min ($\frac{3}{4}$ to 1 gal/min) at the discharge pipe. Based on preliminary tests, this flow rate would provide a burning surface region of nearly half to two-thirds the 2.8 to 3.8 m^2 (30 to 40 ft^2) enclosed by each boom. In all cases, the resulting exposure to flame was felt to be representative of the burning conditions that might be encountered during the burning of oil flowing into a U-shaped boom configuration. During an actual spill, burning oil would likely shift under the influence of wind and currents between different portions of the containment barrier. Both in the field (under actual spill conditions) and in the test-tank configurations used in this project, wind would still be permitted to concentrate the burning oil against various portions of the boom.

At the start of each burn test, air and water temperatures were noted as well as other weather conditions. Each burn test was videotaped, and important physical characteristics of each boom were recorded, including freeboard, skirt depth, size and shape of configuration, ease of handling, flexibility, durability of outer covering(s), etc. These conditions and boom characteristics were noted and recorded throughout each test, recognizing that only qualitative assessments could be made of certain physical conditions or properties in order to avoid unnecessary damage to the boom. During each test the oil flow was stopped briefly at 1 hour and 6 hours into the burn for a closeup inspection of the boom's condition. After these inspections, no other deliberate shutdown was imposed until the full 24 hours of exposure had been completed.

Throughout each burn test, the temperatures measured at each of the thermocouples within the burn area and at or within the boom were recorded with a multi-channel digital thermometer and scanner system. Temperatures were logged automatically at 2-min. intervals for the first hour, at 30-min. intervals for the next 5 hr, and at 1-hr intervals for the remainder of each burn.

At the conclusion of each 24-hr burn, the boom was carefully inspected while it was still in the test tank. It was inspected again after it was removed from the water, and videotape and still photographs were used to document the condition of various outer and inner boom components. The structural integrity, flexibility and potential re-use (or continued use) of each boom were assessed as well.

Houston Test Facilities

Tests funded independently by SWEPI were conducted at the Shell Westhollow Research Center in Houston, Texas, in May, July, and August, 1985. The purpose of the tests was to determine the ability of several booms to contain oil while being towed in waves up to 0.6 m (2 ft) in amplitude. The Shell wave tank used in the tests is approximately 68 m (225 ft) long by 15 m (50 ft) wide by 3.6 m (12 ft) deep and is equipped with a wave generator capable of producing waves up to 0.6 m. The containment

capabilities of each boom were examined using polybutylene pellets with a specific gravity of 0.925 as an oil simulant. In addition, one test was run in July using an oil of 30° API gravity. In that test, it was found that the losses of oil experienced were noticeably less than losses experienced under identical conditions with the pellets. Thus, the pellets provided a conservative substitute for oil.

TEST CONFIGURATION

A total of seven test burns were conducted at Kenai during the summer of 1985 involving the following boom configurations:

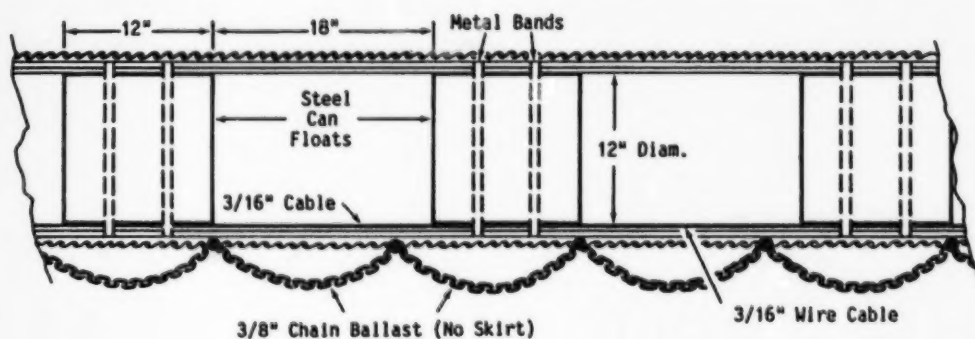
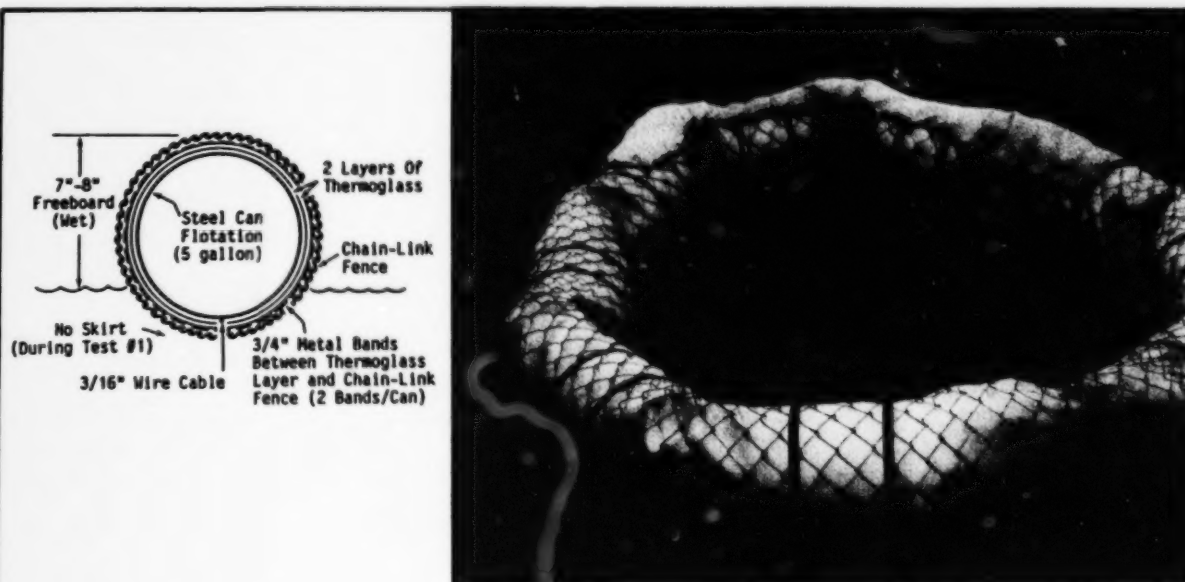
<u>TEST</u>	<u>DATES</u>	<u>BOOM</u>
1	5/28, 5/29	SWEPI Fire Containment Boom (with chain-link outer cover and no skirt)
2	5/30, 5/31	3M Fire Boom Blanket (over Kepner 8" x 12" Standard Boom, bead-filled)
3	6/1, 6/2	Kepner FireGard Boom
4	6/4, 6/5	Globe International PYROBOOM Fire Containment Boom
5	6/8	3M Fire Boom Blanket (over Kepner 14" x 18" Compactible Boom)
6	6/8, 6/9	SWEPI Fire Containment Boom (with 3 experimental test segments including skirt)
7	7/25, 7/26	3M Fire Boom Blanket (over Kepner 14" x 18" Standard Boom, rolled foam log)

In all tests, except No. 5, the boom was exposed to the burning oil for a full 24 hours. In Test No. 5, the 3M Fire Boom Blanket lost significant freeboard at a point where the underlying Kepner Compactible Boom did not retain its normal shape and buoyancy. This failure was not a result of any shortcomings in fire resistance of the 3M Blanket or of the normal functioning of the Kepner Boom. The original Kepner Boom was too long for the available 3M Fire Boom Blanket. It was therefore necessary to cut the metal "compactible" coil of the Kepner Boom, and the boom's structural integrity was destroyed in the process.

The four basic boom configurations (SWEPI, 3M, Kepner, and Globe) as prepared for each of the above seven tests, are illustrated in Figures 2 through 8 (diagrams with English units are directly from the original report).

SUMMARY EVALUATION

Detailed descriptions of each burn test, including plots of peak temperature profiles inside and outside each boom, are contained in the



Abrasion Protection: Chain-link fence placed completely around upper, flotation portion of boom.

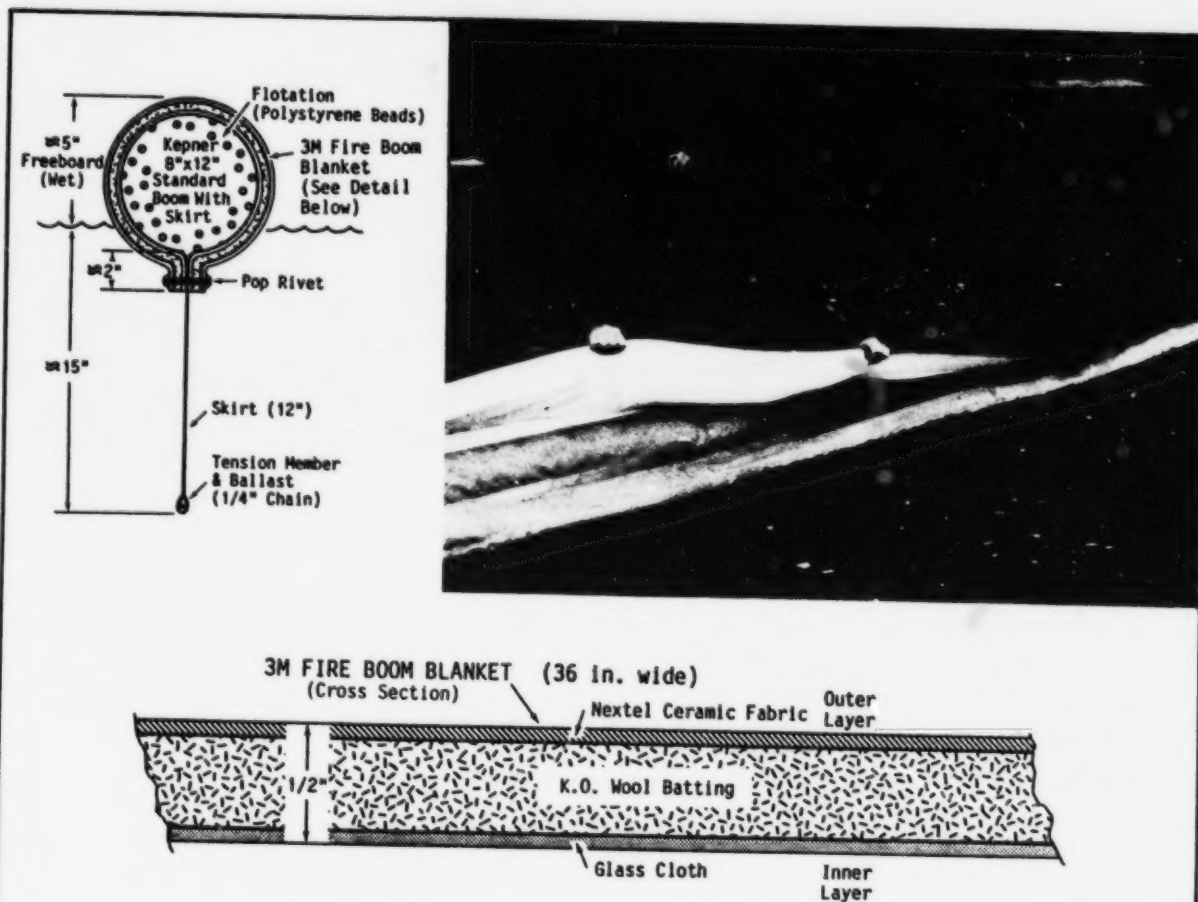
Fire Protection: Two layers of 70 oz. Thermoglass held adjacent to flotation cans with steel bands.

Flotation: 5-gal metal cans, 18 in. apart and attached to 3/16-in. cable.

Skirt: None used in this test.

Tension/Ballast: 3/16-in. cable for tension. Cable plus 3/8-in. chain connected to wire fence for ballast.

FIGURE 2 SWEPI FIRE CONTAINMENT BOOM WITH CHAIN-LINK OUTER COVER AND NO SKIRT (TEST NO. 1)



Outer Layer: #312 Nextel, open-mesh ceramic continuous-filament fabric by 3M, St. Paul, Minnesota. Fabric neoprene-coated.

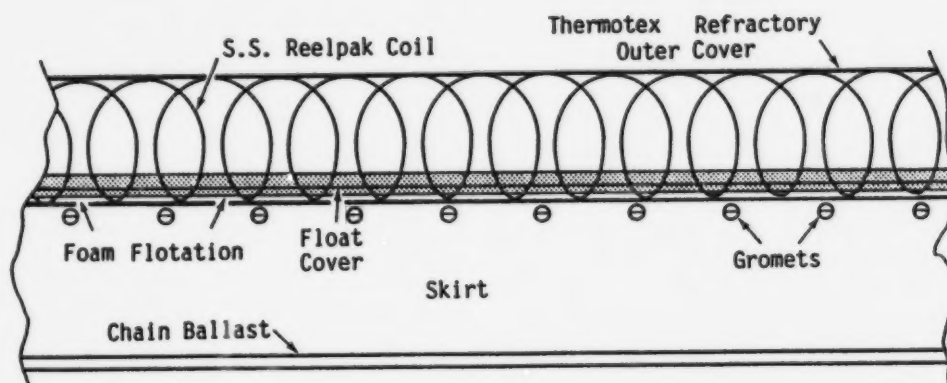
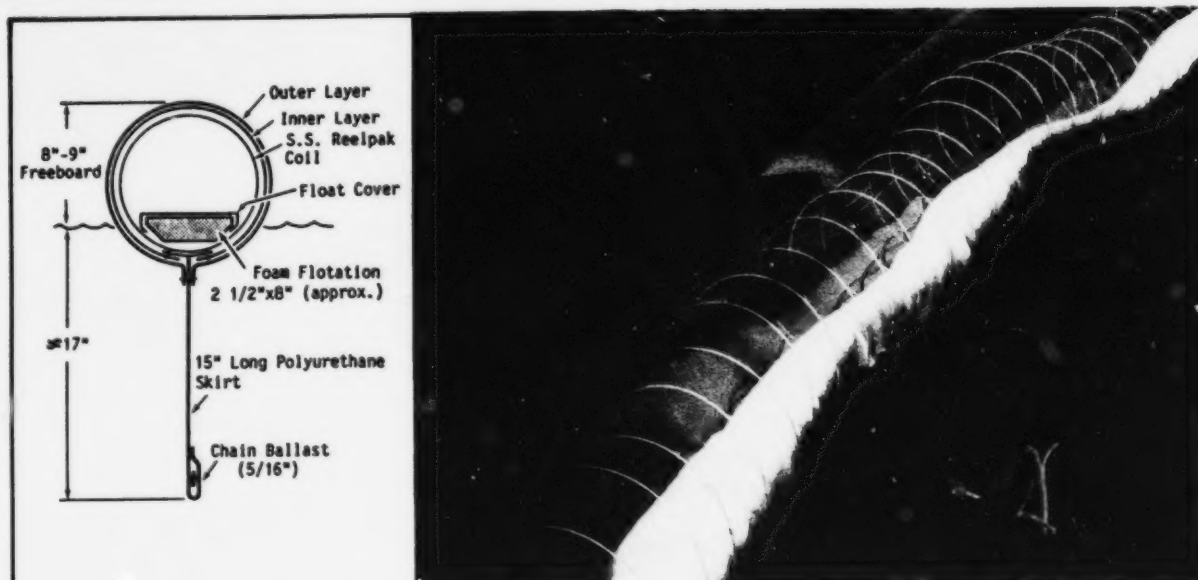
Middle Layer: K.O. Wool, ceramic batting (short staple fibers) by Babcock & Wilcox, Augusta, Georgia.

Inner Layer: Glass Cloth, Style 1583, fiberglass fabric by Schwabbel, White Plains, N.Y.

Connectors: Pop-rivets placed through blanket and skirt material every 12 inches.

Support Boom: Kepner Standard Boom with 8-in. flotation, 12-in. skirt, and polystyrene beads as filler. Fabric cover, 22-oz. PVC. Ballast, 1/4-in. chain. No connector plates used.

FIGURE 3 3M FIRE BOOM BLANKET OVER KEPNER 8" X 12" STANDARD BOOM, BEAD-FILLED (TEST NO. 2)



Abrasion Protection: Outer and inner covers treated with an abrasion-resistant polymer coating.

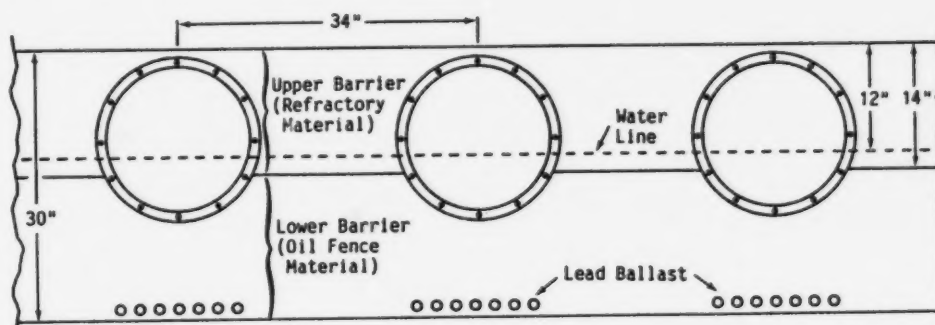
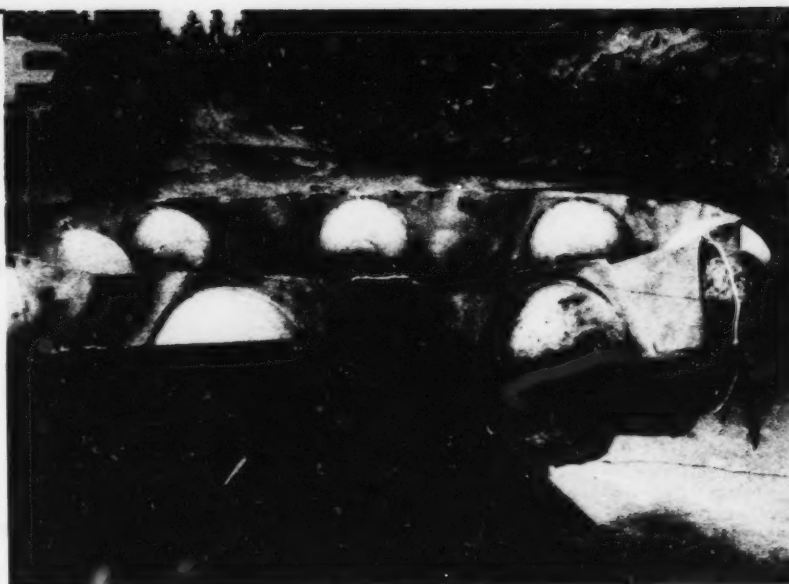
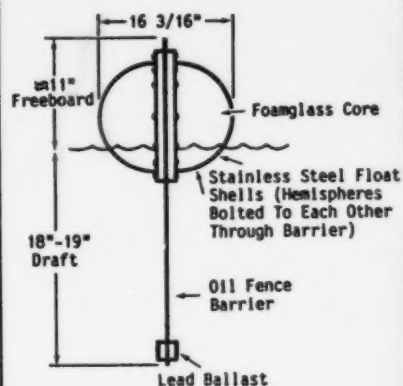
Fire Protection: Two layers of Thermotex refractory fabric suspended over stainless steel coil. Flotation wrapped with fiberglass fabric.

Flotation: 2½-in. x 8-in. multiple-layer, closed-cell Resistex foam flotation running entire length of test boom. Flotation wrapped with fiberglass fabric.

Skirt: 15-in. skirt made of 22-oz. PVC fabric.

Tension/Ballast: Bottom-tensioned and ballasted with 5/16-in. chain. No connector plates used.

FIGURE 4 KEPNER FIREGARD BOOM (TEST NO. 3)



Abrasion Protection: Stainless-steel shells for flotation. Upper refractory material (above water) impregnated with RTD silicon rubber.

Fire Protection: Heat-resistant, closed-cell foam glass surrounded by stainless steel for floats. Fiberfrax fabric (with inconel wire and silicon rubber treatment) in upper half of boom.

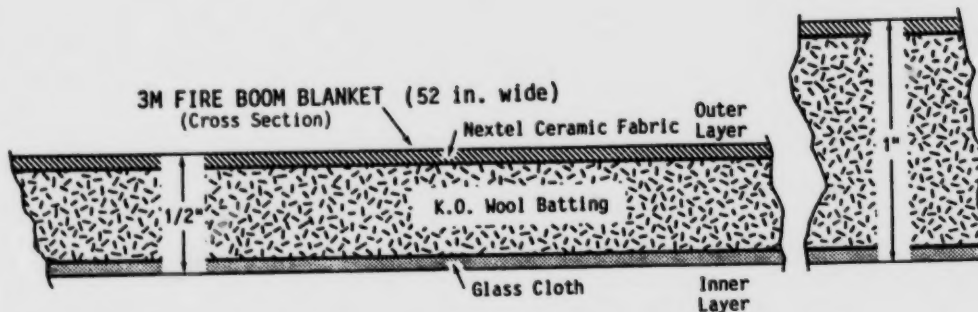
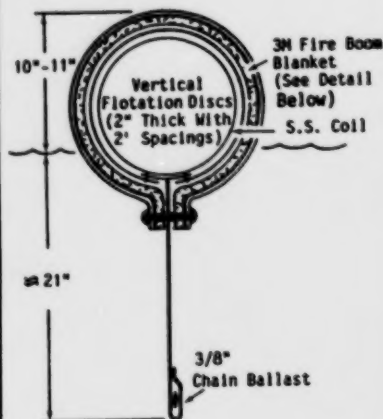
Flotation: Hemispheres (16-in. diam.) at 34-in. spacings bolted together through boom fabric. Shells and buoyant cores easily removed and reused.

Skirt: Urethane-coated conveyor-belt material.

Tension/Ballast: Fence-boom configuration provides distribution of tension throughout upper wire-reinforced refractory material and lower conveyor-belt material. Ballast provided by lead discs averaging about 2 lb/ft.

FIGURE 5

GLOBE INTERNATIONAL PYROBOOM (TEST NO. 4)



Outer Layer: #312 Nextel, open-mesh ceramic continuous-filament fabric by 3M, St. Paul, Minnesota. Fabric neoprene-coated.

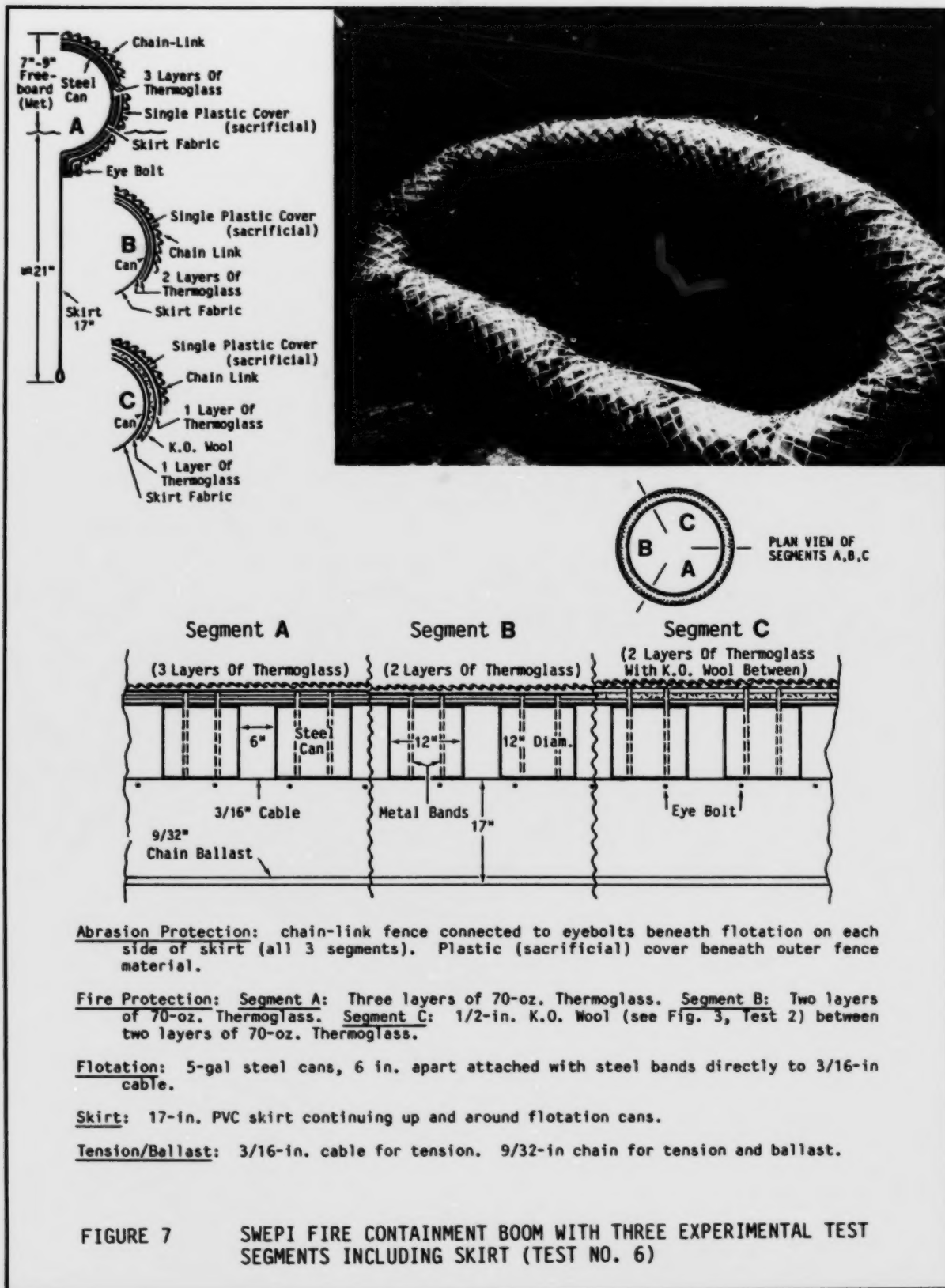
Middle Layer: K.O. Wool, ceramic batting (short staple fibers) by Babcock & Wilcox, Augusta, Georgia. Half of boom had 1/2-in. batting, and half had 1-in. batting.

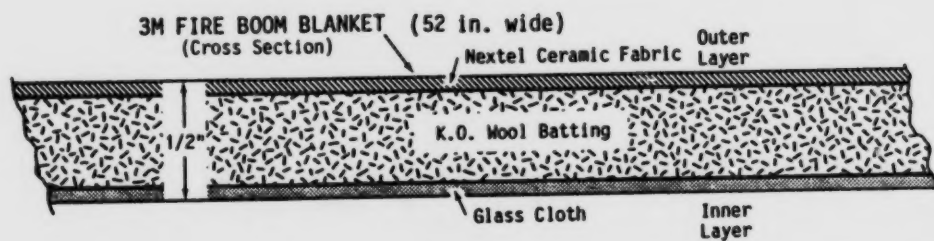
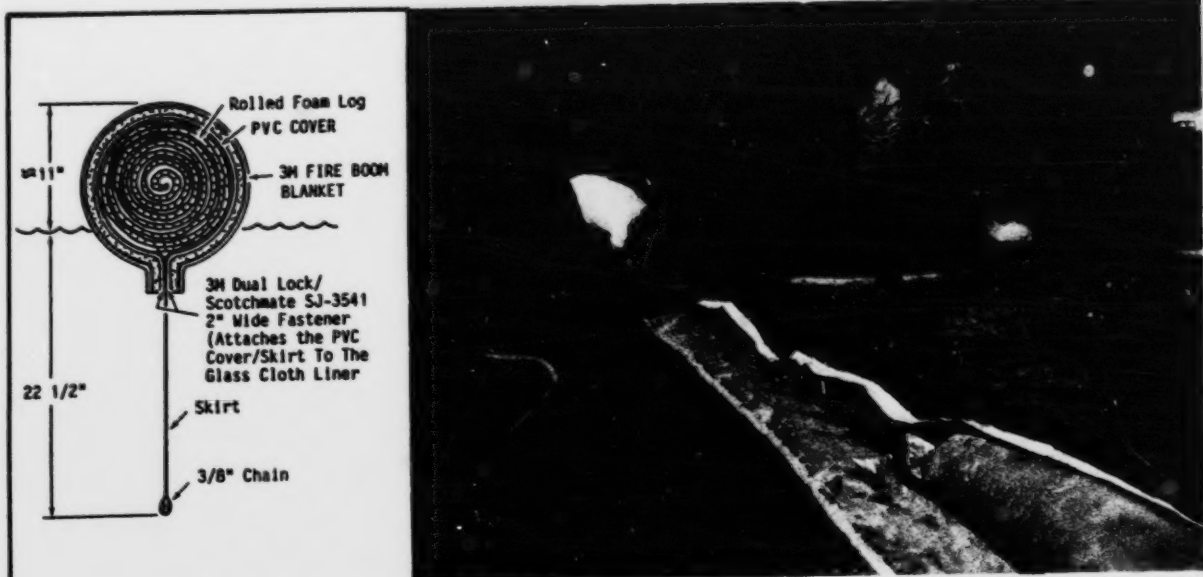
Inner Layer: Glass Cloth, Style 1583, fiberglass fabric by Schwabbel, White Plains, N.Y.

Connectors: Pop-rivets placed through blanket and skirt material every 12 inches.

Support Boom: Kepner Compactible Boom with 14-in. flotation, 18-in. skirt, and PVC-fabric-covered coils. Flotation provided by air inside covered coils, plus 2-in. thick polyurethane foam discs spaced 2 ft apart. Ballast, 3/8-in. chain. No connector plates used.

FIGURE 6 3M FIRE BOOM BLANKET OVER KEPNER 14" X 18" COMPACTIBLE BOOM (TEST NO. 5)





Outer Layer: #312 Nextel, open-mesh ceramic continuous-filament fabric by 3M, St. Paul, Minnesota. Fabric neoprene-coated. One 7½-ft side of boom covered with light-gauge, woven stainless-steel mesh for experimental purposes.

Middle Layer: K.O. Wool, ceramic batting (short staple fibers) by Babcock & Wilcox, Augusta, Georgia.

Inner Layer: Glass Cloth, Style 1583, fiberglass fabric by Schwabbel, White Plains, N.Y.

Connectors: 2-in.-wide strips of 3M Dual Lock/Scotchmate (SJ-3541) fasteners (half of fastener strip glued to PVC cover beneath flotation, other half glued to inner glass-cloth liner of blanket). Fastener strips run full length of boom.

Support Boom: Kepner Standard Boom with 14-in. flotation, 18-in. skirt, and PVC-covered, rolled foam log for flotation. Ballast, 3/8-in. chain. Connector plates, standard Kepner extruded aluminum plates, shortened to fit under blanket.

FIGURE 8 3M FIRE BOOM BLANKET OVER KEPNER 14" X 18" STANDARD BOOM, ROLLED FOAM LOG (TEST NO. 7)

original project report available from ACS, Anchorage, Alaska (Spiltec, 1986). Table 1, however, presents a summary of the results from both the Houston wave and current tests and the Kenai burn tests. It is recognized that some of the assessments made are subjective, therefore relying upon the judgement of personnel conducting the tests and preparing the text of this report. Every effort has been made to present the results of the tests as fairly and as accurately as possible, while avoiding the very natural tendency to make comparisons between the containment systems. Any meaningful comparison would have to reflect the different performance objectives and the modes of use for which each system might be selected, as well as storage and individual cost considerations.

For example, a particular containment system might involve materials that are highly resistant to abrasion; however, such characteristics may not be necessary if the system is never expected to be exposed to ice, debris, or frequent rough handling. Under another set of conditions, a potential user may need a system that must be deployed and recovered frequently with a very low probability of ever being needed for the containment of fire. The durability and ease of handling in this case would represent important characteristics against which the system's resistance to fire would have to be weighed. These and many other factors, such as the expected duration of any fire and the seas under which containment would be required, help emphasize the fact that no one system is necessarily best for all potential fire containment situations.

Because of the many operational considerations that go beyond the oil containment and fire resistance characteristics of a boom, Table 2 is provided as a summary of other considerations pertinent to each of the containment systems as tested. One must keep in mind that the assessments contained in Tables 1 and 2 are based on the specific containment system(s) provided by each manufacturer. In some cases, the manufacturer is capable of providing variations on the size, shape, and/or material used in their particular product. In at least three of the four fire containment systems reported on here, the manufacturers have already indicated that modifications are underway to improve their respective products.

In conclusion, the results of this project suggest that:

- o Existing commercially available fire containment systems do exist with the potential of containing burning oil for at least 24 hr;
- o Such systems are sufficiently durable and portable to be transported to and deployed at the scene of an offshore or nearshore spill quickly and efficiently; and
- o These same systems can be expected to contain oil at least as effectively as most conventional open-ocean booms under waves and current conditions typically attempted with mechanical containment devices.

REFERENCE

Spiltec, 1986. Test and Evaluation of Fire Containment Boom. Prepared under contract to Shell Western E&P Inc., for Alaska Clean Seas, Anchorage, AK.

TABLE 1

BOOM PERFORMANCE SUMMARY

ACS KENAI 24-HOUR BURN TESTS

CRITERIA	PYROBOOM			SMEPI		FIRE BOOM BLANKET	
	FIRECARD TEST 3 (2 fabric layers on coil)	TEST 4 (single-layer fence boom)	TEST 1 (2 layers, no skirt)	TEST 6 (3-segment experimental test)	TEST 2 (on 8" x 12" solid-fill boom)	TEST 5 (on 14" x 18" coil boom)	TEST 7 (on 14" x 18" solid-fill boom)
OIL CONTAINMENT 24-hour Burn Test (static test)	No loss of oil	No loss of oil	No loss of oil	No loss of oil	No loss of oil	Lost oil (malfunction) in support boom	Minor loss of oil (less than 1 gal)
PERFORMANCE DURING BURN External Surfaces	Noticeable loss of resistance to abrasion. Fully capable of containing burning oil, though dry and brittle on upper surfaces.	Rapid deterioration of upper refractory material. Baked silicon rubber coating flakes off with minimal abrasion. Strength retained by wire structure. Still impermeable to oil.	No visible damage. Fabric continually wet and flexible. Slight increase in stiffness due to burn residue buildup. Slight reduction in fabric abrasion resistance. No damage to chain link fencing.	No visible damage in any of the 3 experimental segments. All surfaces wet and flexible. Usual thin buildup of burn residue and slight reduction in fabric abrasion resistance. No damage to chain link fencing.	No visible damage. Slight decrease in resistance to abrasion. Fabric continually wet and flexible. Slight buildup of burn residue.	No visible damage up to point of termination (about 1 hr. burn time).	Significant discoloration and localized brittleness over one 2- to 3-ft section of boom. All other surfaces in excellent condition (wet and flexible).
Internal Components	Second layer also less resistant to abrasion. Fabric impermeable to oil flow at water line, though dry and easily punctured above water line.	K.A.	Second layer of fabric oil-stained in places, though wet, flexible and in excellent condition. No significant reduction in abrasion resistance.	Second layer of Segment B discolored and slightly brittle. Middle K.O. Wool layer in Segment C questioned. All layers in excellent condition. Segment A with 3 layers in excellent condition.	K.O. Wool in good condition, though mushy and easily torn/displaced if exposed to vertical stresses. 7-1/2" thick steel liner in excellent condition.	Unsuccessful alteration of coils in Kapner Boom caused mechanical failure of support for blanket.	Same as Test No. 2, except for thermal stress in localized region mentioned above.
Floitation/Freeboard	Fabric-wrapped foam flotation in excellent condition. No loss of freeboard.	Steel shells and foam glass filler in excellent condition though foam was brittle and cracked. No loss of freeboard.	Steel flotation cans undamaged. No loss of freeboard.	All flotation cans undamaged (no loss of freeboard). Slight damage to steel flotation cans in Segments B and C. No thermal stress on A (3 layers).	Kapner Boom as support for flotation in excellent condition. No signs of thermal stress.	Rapid loss of flotation and freeboard.	Half-dome of 2- to 3-ft of Kapner Boom Reduction in freeboard from 11" to 3". Remaining portion of Kapner boom like new (no reduction in freeboard).
Continued Burn Potential (under similar, static test conditions)	Good	Good	Good to Excellent	Excellent for Segment A and for Segment B. Fair for Segment C.	Excellent	None	Of questionable value (1 to 2 hr at most)
Reusability	Highly unlikely. Coil/flotation components could be reused.	Highly unlikely. Flotation system and skirt would be reused.	Highly unlikely. Flotation system could be reused.	Possible for 2nd and 3rd layer of Segment A. All chain-link barrier and flotation system could be reused.	Highly unlikely for blanket. Kapner Boom was oil stained but definitely reusable.	None	None
Recovery	Relatively light and easy to remove. Easy to remove fabric covers.	Relatively light and easy to remove. Medium to heavy. Easily attached for deployment or recovery.	Difficult. Water-saturated fabric quite heavy.	Difficult. Water-saturated fabric quite heavy.	Difficult. Water-saturated fabric quite heavy.	Difficult. Water-saturated and damaged.	Difficult. Water-saturated and damaged.

SMEPI HOUSTON WAVE TANK TESTS

CRITERIA	PYROBOOM		SMEPI		FIRE BOOM BLANKET	
	FIRECARD	TEST 4	TEST 1	TEST 6	TEST 2	TEST 5
OIL CONTAINMENT Houston Wave Tank (2-ft waves/ 0.5 kt current); same tests conducted with oil simulant)	Very minor oil loss. Good towing and wave riding characteristics to greater than 1 kt.	Some oil loss. Above 0.7 kt, significant oil loss. Above 0.8 kt, boom unstable.	Very minor oil loss Good towing and wave riding characteristics to greater than 1 kt.	Very minor oil loss Good towing and wave riding characteristics to greater than 1 kt.	Very minor oil loss	Blanket does not reduce oil containment of support boom. Blanket does reduce freeboard of support boom (2" to 3" reduction with Kapner 14" x 18" Standard Boom). No noticeable reduction in wave-riding or towing characteristics.

TABLE 2
FIRE CONTAINMENT BOOM ASSESSMENT: OTHER CONSIDERATIONS

CONSIDERATION	FIRECARD	PYROBOOM	SWEEP	FIRE BOOM BLANKET
Pre-burn Resistance to Abrasion	Thermotax refractory outer cover provides tough, smooth surface. Continuous contours minimize tendency for snagging.	Stainless steel floats are highly resistant to abrasion, offering some protection to fabric as well. Coated refractory material with Inconel wire provides good abrasion and puncture resistance. External floats may increase potential for snagging.	Uncoated Thermoglass layers are protected by sacrificial plastic cover and rugged chain-link fence barrier. Though strong and resistant to abrasion, fence material may increase potential for snagging.	Neoprene-coated Nextel outer fabric provides durable, smooth surface. Continuous contours minimize tendency for snagging.
Ease of Handling (4 Weight)	Lightweight and easy to deploy, operate and recover. (Open Harbor, as tested = 3.3 lb/ft, dry)	Moderately heavy. Convenient handles for ease in deployment and recovery. Irregular surface can make handling awkward in some situations. (Weight, as tested = 7.5 lb/ft, dry)	Moderately heavy. Chain-link barrier can be used for handling during deployment and recovery. (Weight, as tested with 3 layers = 7 lb/ft, dry; 11 lb/ft, wet)	Relatively light. Blanket can be attached easily with grommets or with 3M Dual Lock/Scotchmate fasteners. Boom must be prepared with fastening system in advance. (Blanket weight 52" wide = 2.8 lb/ft, dry; 22.4 lb/ft, wet).
Tensile Strength	20,000 lb (function primarily of bottom tension member)	Total tensile strength is approximately 46,000 lb.	20,000 lb. (function primarily of bottom tension member)	Blanket does not provide significant additional tensile strength (depends on boom used).
Compactibility	4:1	0	0	0
Storage	Normally store on reel. Keep dry and covered. 0.18 ft ³ /ft of length.	200 to 220 ft ³ /100 ft of length. Estimate: 250 ft per 8"x10" reel or 1000 ft per 40"x8"x8' van. Keep covered.	Estimate: 600 ft per 40"x8"x8' van. Keep dry and covered.	12 ft ³ /25 ft length (52" wide blanket only). 1,000 ft per 40"x8"x8' van with Kepner 14"x18' boom.
Maintenance & Repair	Low maintenance; easily repaired since protective layers are removable. Replacement covers available from manufacturer. Coil and flotation reusable.	Floats, connectors and all below-water materials are reusable. Pre-punched refractory material available in coils from manufacturer @ 20¢ to 25¢ total boom cost.	Floats, connectors and below-water parts reusable. Thermoglass and other protective layers commercially available. Fabrication and field maintenance personnel available from manufacturer in Alaska.	If damaged, return to manufacturer. If used, dispose of in accordance with federal/state regulations. Not reusable if wetted.
Estimated Cost (FOB factory 12/85)	\$200,000/1,000 ft (without reel)	\$165,000/1,000 ft	\$125,000/1,000 ft	\$157,000/1,000 ft (blanket only)

LASER IGNITION OF ARCTIC OIL SPILLS
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ABSTRACT

The design of a system which will enable helicopter deployment of the Laser Ignition of Arctic Marine Oil Spills technique, introduced at last year's seminar, is presented. The design includes methods for aligning and focusing the lasers, powering and cooling them and the associated electronics, stably pointing the lasers at an oil pool in the presence of helicopter vibrations, rangefinding, controlling the system, and mounting the components in an airworthy manner.

INTRODUCTION

Over the past four years, a novel dual-laser approach for ignition and burning of Arctic oil spills has been developed under the sponsorship of Environment Canada^{1,2,3}. The process may be summarized as follows: A continuous-wave (CW) carbon dioxide laser is used to heat a portion of the surface of an oil pool to its flashpoint temperature and simultaneously establish a thermal field within the oil which will not quench a nascent flame. A focused, pulsed laser beam then provides energy which creates a momentary "spark" above the oil surface to ignite a fire. Previous work has shown that, to ensure ignition of properly preheated oil, the pulsed laser should provide a fluence of at least 10 J/cm^2 . In addition, to minimize the preheating time required to start a self-sustaining fire, it is generally desirable to use a CW laser

providing as much power as is possible. Presently available lasers suitable for helicopter mounting supply up to 1000 W.

To utilize this technique for ignition of oil in an Arctic environment from an airborne platform, the sequence of events shown in Figure 1 must be followed. The sequence begins with "target acquisition": The system operator locates the position on the oil pool at which the lasers are to be aimed, points the lasers at that position, and confirms that the beams are in fact where the operator thinks they are pointed. The pulsed laser beam is then focused to the required fluence at the oilpool surface by adjusting the separation between two optical elements comprising a reverse Cassegrainian telescope. Next, laser firing commences and continues until a self-sustaining fire is established. During this period, the beams must not be allowed to drift or oscillate over such a large region as to preclude efficient heating of the oil.

Clearly, an air-deployable Laser Ignition of Oil Spills (LIOS) system requires numerous interacting components which must:

1. Include a pulsed laser which is focused to provide sufficient fluence to ignite, from a distance, fires on preheated oil pools;
2. Include a CW CO₂ laser producing up to 1000 W of power which is optically configured to irradiate an oil pool with the required preheating intensity;
3. Incorporate a means of aligning and holding the laser beams on target despite helicopter movements and vibrations;
4. Provide sufficient power and cooling capability to operate all of the components;
5. Be installable in a Sikorsky S61 or comparable helicopter without affecting airworthiness or safety; and
6. Be operable by an aircraft maintenance technician.

The design of such a system has now been completed⁴, and is described herein.

OPTICS

As illustrated in Figure 2, an optical layout has been designed which incorporates in one integral platform the two lasers and optical trains for focusing, rangefinding, and beam alignment. Except for the lasers, all of the components are mounted on a rigid optical table, component #1. The two lasers (components #15 & #16) lie on a shelf below the optical table, and their beams are reflected to the table surface by several small mirrors (indicated as components #9 & #10). This entire structure is isolated from high-frequency helicopter vibrations by suspending it on damped springs.

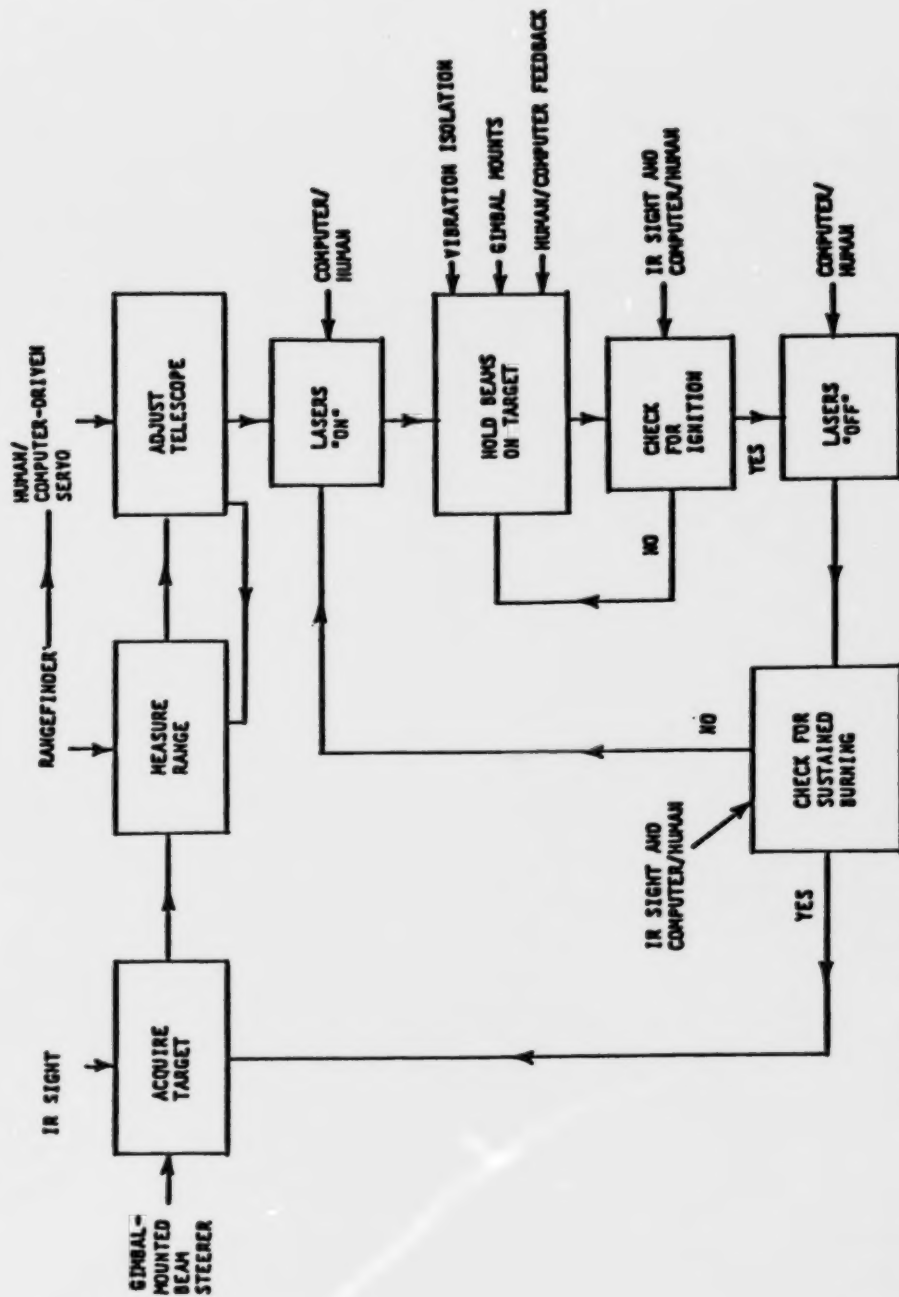


FIGURE 1 - LASER IGNITION SEQUENCE

COMPONENTS

1. Optical Breadboard
2. Rangefinder (Option B)
3. IR Scanning Radiometer for Targeting System
4. Gimbal Mount for 10-12 in. Optic
5. 12 in. Diameter Gold Coated Mirror with 2 in. Hole (Option A)
12 in. Diameter Dichroic Pyrex Window
6. -9 in. F.L., 1.5 in. Diameter AR Coated GE Lens mounted in 10 in. Diameter Ring
7. 2 in. Diameter, AR Coated (at 10.6 μm) GE Flat mounted in 14 in. Diameter Ring
8. 2 in. Gold-Coated Mirror mounted in 14 in. Diameter Ring
9. Pulsed Laser Beam Steering Mirror
10. CW Laser Beam Steering Mirror
11. 10 in. Diameter, 60 in F.L. Gold-Coated Parabolic Mirror
12. 4 in. Linear Translation Stage
13. DC Drive Motor and Electronics for Feedback Control
14. Beam Targeting System
15. CW Laser
16. Pulsed Laser
17. CW Laser Beam Diverging Lens

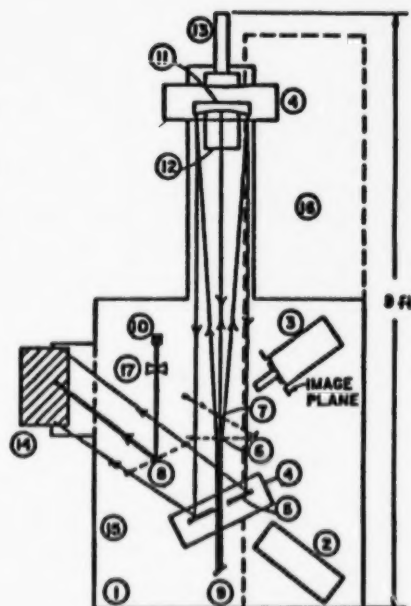


FIGURE 2 - LAYOUT OF L.I.O.S. OPTICAL SYSTEM

Pulsed Laser Selection and Focusing

The pulsed laser (component #16) will be a Lumonics Model TEA-103, selected on the basis of its weight, size, beam quality, energy per pulse, repetition rate, structural integrity, power requirements, efficiency, and cost. The laser will be operated in the unstable resonator configuration, providing 8 J per pulse with a nominal beam divergence of 0.8 mrad.

Assuring that the pulsed beam is focused at the surface of the oil pool to a fluence of at least $10\text{J}/\text{cm}^2$ is the most critical optical task in this program. The beam, after being transmitted to the table top, is focused by a reverse Cassegrainian telescope, reflected to a pointing mirror, and thence to the oil pool. To minimize the size, and thus the cost, of the focusing optics, the telescope has been designed to operate at the minimum acceptable helicopter hovering altitude of 20 m. To optimize the ground area which can be covered from a fixed hover (as constrained by the divergence of the CW laser, discussed later) a capability to continuously vary the effective focal length of the telescope between 20 and 30 m has been included.

The path of the pulsed laser beam is shown in Figure 2 as directed lines. It first passes through a small hole in reflector #5 (the full function of which is discussed later), and impinges upon an anti-reflection coated, -22.8 cm focal length, 3.8 cm diameter germanium lens (component #6), which causes the beam to diverge. The diverging beam passes unaffected through a germanium flat, also coated so as to be non-reflective at the laser wavelength (component #7, discussed later) and, after having expanded to a diameter of about 20 cm, strikes the movable 152.4 cm focal length, 25.4 cm diameter focusing mirror (#11). The beam is reflected back along its original path and, now slightly converging, is directed by component #5 onto the pointing mirror #14 and subsequently onto the oil pool. The distance from the focusing mirror to the location at which the beam achieves its minimum diameter can be altered by changing the separation between that mirror and the diverging lens. To vary this effective focal length from 30 to 20 m, the separation between the two elements should range from 1.377 to 1.421 m. For this purpose, the focusing mirror is mounted on a motorized translation stage (#12).

The focusing of the laser will be controlled by either of two methods: A) By using the focusing mirror to form a visible/infrared image of the oil pool, and varying the separation between the two telescope components until this image is in focus; or B) By measuring directly the distance between the telescope and the oil pool, and using it to calculate the appropriate component separation. Option A is called passive focusing, option B is active. The optical layout of Figure 2 has been designed to accommodate either scheme.

With passive focusing, the image formed is comprised of radiation from scattered sunlight and infrared energy emitted in response to heating by the lasers. It therefore has a fairly broad

spectral distribution, containing energy at wavelengths ranging from the visible to the far-infrared, which propagates along nearly the same path as the pulsed laser but in the opposite direction. Most of this energy is split from that path by the germanium flat #7, which, although coated to transmit energy at $10.6\mu\text{m}$ without reflection, is highly reflective for wavelengths shorter than about $5\mu\text{m}$. When focused, a crisp image of the oil pool will be formed at the image plane indicated near component #3. The image plane is located at a distance equal to the sum of the focal length of the diverging lens and the optical element separation. Therefore, by the principle of reversibility, the laser will be focused on the oil pool when the image of the pool is in focus. A focus analyzer (component #3), similar to those used in self-focusing zoom lenses, could be located at the image plane and used to drive a servo motor (component #13) to move the imaging optic in the proper direction to optimize focusing. Although this passive focusing technique is conceptually simple, its accuracy and cost cannot be determined without experimentation.

The active focusing system utilizes a device to measure the distance to the oil pool, a lookup table or equation from which to determine the proper telescope component separation for the measured range, and a controller to set that position. The most accurate means currently available for measuring distances is to use a laser rangefinder, such as the Canadian manufactured Optech Model 60. This device uses a diode laser, radiating at a wavelength of $0.9\mu\text{m}$, to measure distances up to 150 m with a 30 cm accuracy, which is sufficient for our needs. According to the manufacturer, it will have no difficulty in measuring the distance to an oil pool even when receiving only backscattered laser radiation from a 45° angle of incidence. If used, the rangefinder will be incorporated into the optical system by substituting a dichroic pyrex window, coated to reflect in excess of 95% of the incident CO_2 laser radiation at $10.6\mu\text{m}$ but transmit more than 70% of the near-ir radiation used by the rangefinder, in place of the simple gold-coated pyrex mirror used in passive focusing to direct the beam to the pointing mirror (component #5). By positioning the rangefinder as shown it can be aligned colinearly with the pulsed laser. To be used as an automated focusing system, the distance measured by the rangefinder will be fed into a computer which calculates the appropriate focusing mirror position and drives a servo to move the mirror as necessary.

CW Laser Selection and Alignment

On the basis of its size, weight, ruggedness, cooling requirements, power requirements, gas consumption, ease of operation, and cost, the Laser Corporation of America (LCA) Falcon 800 was selected as the CW laser. Its beam emerges from the laser head with a diameter of 32 mm and has a far field divergence of 1.5 mrad full angle. It is capable of producing up to 1000 W.

Previous work¹ has shown that, when incident upon the oil surface, the CW laser beam should describe a circle having a diameter

between about 6 and 12 cm, or an area between 28 and 115 cm². For this constraint to be satisfied from a 20 m hover, the beam divergence must be increased over that which the laser provides naturally. It has been found that the maximum ground area can be covered when the divergence is increased by passing the beam through a -20 m focal length lens. Then, the beam can be aimed over vertical angles ranging from 0 degrees (straight down) to 49 degrees, corresponding to the slant ranges of 20-30 m discussed above, without the irradiated area at the oilpool surface becoming excessive.

The CW and pulsed lasers are aligned colinearly without substantial power losses by using the "hole" in the pulsed beam, formed by the hole in reflector #5, as an area in which to mount additional optical elements. In particular, the relatively small diameter CW laser beam is reflected from a mirror mounted within the hole, indicated as component #8. This mirror is held in place by three small prongs which extend from a ring having a diameter large enough to surround the expanded pulsed beam, thereby minimizing power losses to the optical holders. Both laser beams are then directed to the oil pool by mirror #14.

POWER AND COOLING

The Falcon 800 laser consumes 21 kW of electricity to supply 1 kW of laser power; cooling water is used to reject the 20 kW of waste heat. In a helicopter there can be no external supply of water, so the water must be air-cooled. The simplest way to cool the water, by using a commercially manufactured heat exchanger able to dissipate the full 20 kW, was found to be also the best solution. Assuming an ample supply of Arctic air is available at 0-5°C, then three Lytron Inc. Model 6321G3 heat exchangers, will adequately cool the water. These units are small, lightweight, and inexpensive.

The installation of the LIOS system requires the availability of a large amount of electrical power for the CW laser (21 kVA). The power requirements of all the other electrical equipment associated with the LIOS system, and the pulsed laser combined do not approach this level of power demand. In fact, the sum of the power required by all units not including the CW laser will be less than 4 kW, which can easily be satisfied by existing aircraft power supplies.

For the S-61R helicopter, there is a 300A, 28V DC generator, and two 20 kVA, 115V AC, 400 Hz generators. An existing APU is mechanically linked to the rotorcraft gearbox for use as a starter unit. Although its power output would be sufficient for the needs of this system, installation of a generator would require major modifications to the helicopter. Typical aircraft operations will require roughly 200 A DC, and approximately 28 kVA AC power. This will leave about 1 kW of DC power and 4 kW of AC power, accounting for the fact that electrical loading should not exceed 80% of the generator capacity as specified in the Canadian Department of Transport Engineering and Inspection Manual⁵.

All of the electrical units will require power in the standard 120V, 60 Hz AC format, and hence, either power inverters or converters will have to be utilized. Typical efficiencies of these units are 70% for inverters (AC to DC), and somewhat less for the power converters (AC to AC) -- perhaps 50-60%. This will dictate a power availability of 7 to 8 kW. This load could well be satisfied by the aircraft power systems, if the unnecessary aircraft equipment were shut down during the operation of the LIOS system. However, the requirement of 21 kVA power for the CW laser clearly specifies that some sort of auxiliary power be available. Installation of an Auxiliary Power Unit (APU), coupled to a suitable AC generator, can easily supply all the power requirements of the CW laser, and perhaps some of the associated electronics as well. The CW laser requires AC power with the following characteristics:

230 VAC; 3 phase; 60 Hz.

Standard aircraft APU units are available from 28 HP (21 kW) up to 150 HP (112 kW). The typical APU's, however, are in the 40 HP (30 kW) to 80 HP (60 kW) range. Assuming a generator efficiency of 75%, the 21 kVA power requirement would translate to a power capacity of 28 kVA required from the APU.

The Turbomach Division of Sundstrand manufactures a complete line of compact, lightweight APUs for airborne systems. A generator is necessary to convert the mechanical output of the APU into electrical power. Such generators are available from Bendix. An alternative would be to modify a ground-based electrical power unit for mounting in the helicopter.

Installation of an APU complicates matters from the point of view of airworthiness requirements compliance; many safety measures concerning airworthiness must be satisfied, such as fire protection, a protective housing for the APU, and ventilation of the housing.

Since no APU installations of this capacity have been developed or approved under Supplemental Type Approvals (STA) in Canada or Supplemental Type Certificates (STC) in the U.S., one such installation will have to be developed for this particular system. In order to avoid major helicopter modifications, the system must be independent of aircraft fuel supply and main power bus. As such, this design must include a separate fuel system and, as indicated above, the precautions necessary to maintain airworthiness, though complex, must be implemented.

The generator, fuel tank, and fire extinguishing system are off-the-shelf items which may be acquired from a multitude of suppliers. The APU housing, ventilation system, and refuelling system will have to be custom designed. Restrictions on the design will be dictated by the APU components chosen and helicopter cabin layout.

TARGETING SYSTEM

The output of both lasers is to be directed by a targeting mirror onto a selected oil pool. The laser beams can drift off target due to the combined effects of high frequency helicopter vibration and low frequency gross helicopter motion. The laser targeting system must compensate for the latter, keeping the laser beams on target for periods of up to 30 seconds with a centroidal drift not exceeding 2 cm. For a target range on the order of 30 m, this requirement translates into an angular deviation of 0.67 milliradians, or about 2 arc-minutes.

The basic components of the targeting system, as shown in Figure 3, are: a sensor that collects the target radiation and converts it to an electrical signal; signal processing electronics that process the sensor output signal to produce pointing error signals; a movable platform that permits isolation from disturbances to the pointing system and allows the sensor to compensate for helicopter motion; and a servo and stabilization system to control the platform position.

The large targeting mirror is mounted on the movable platform. Since the rotation of the laser beam about its axis of propagation is inconsequential in this application, the platform will be biaxial, consisting of an azimuth and an elevation stage, both driven by DC motors. The target should be stationary, have good optical contrast, and should be invariant with respect to rotation. These requirements are fulfilled by the thermal radiation emitted by the laser-heated oil spot. An infrared sensor that detects this radiation will be used to generate appropriate error signals to control the motion of the rotation stages.

Previous experiments¹ have shown that the oil temperature in the zone of laser irradiation exceeds 100 °C. while outside the zone the temperature is about half as high. These tests also showed that the oil takes from 1 to 2 seconds to reach its maximum temperature when irradiated with the CO₂ laser. Thus the laser-heated oil spot can provide a distinctive thermal signature for about a second, which should be ample time for the targeting system to react to shifts in the laser line-of-sight.

The choice of an infrared tracking system depends on performance, cost, and availability. A survey of infrared tracking schemes showed that an imaging tracker is the best choice for LIOS. An imaging tracker uses one or more detectors which produce video signals by means of a linear raster scan of the target scene. Examples of imaging sensors are TV cameras, linearly-scanned detector arrays, and two-dimensional electronically-scanned arrays. The video information is processed digitally to generate error signals proportional to the position of the target in the video image.

The imaging tracker consists basically of the infrared sensor and the signal processing electronics. A good candidate for the former is the Inframetrics Model 525, a scanning infrared radiometer that provides a TV-compatible video output. This instrument will be used to sense infrared radiation in the 8-12 μ m range. This range is

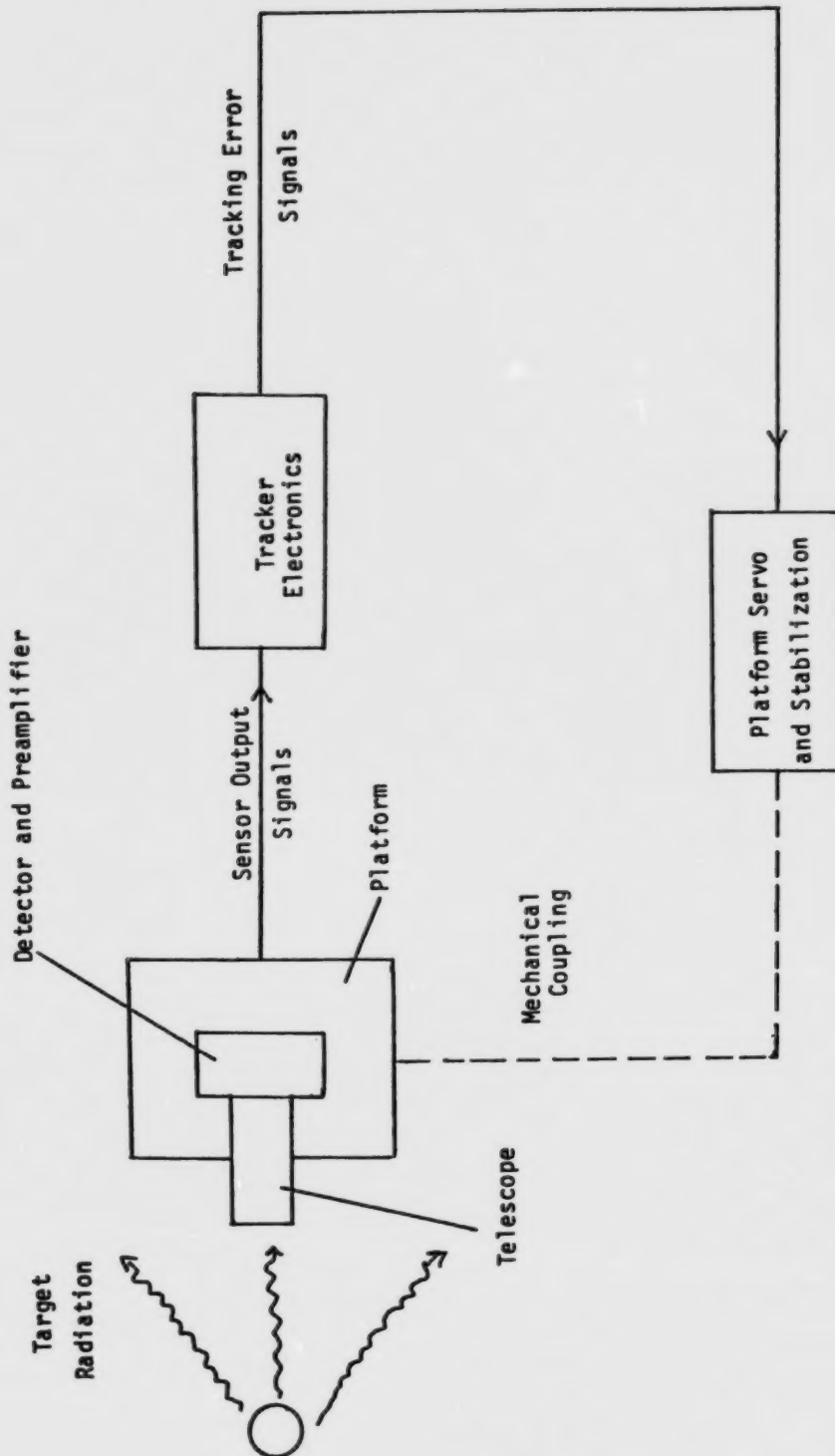


FIGURE 3 - TARGETING SYSTEM COMPONENTS

used instead of the 3-5 μm band because the target signal is stronger and there is less interference from solar radiation in this band.

The scanning radiometer is shown as component 3 in Figure 2. With this arrangement, the infrared image of the oil pool is aligned with the optical axis of both lasers. Motion of the targeting mirror results in a displacement of the scanner's field of view. The anti-reflection coated Ge flat minimizes the effect of backscattered laser radiation on the infrared image.

The video signal from the infrared scanner is processed by a DBA Systems Model 606 video tracker, which has a number of features that make it useful in a tracking application. For example, it can generate and display crosshairs superimposed on the infrared video image indicating the null tracking point. One can choose between either edge or centroid tracking modes. The tracker provides both analog and digital error signal outputs for ease of interfacing with servo components. An auxiliary video input is provided to enable one to mix externally generated signals with the composite video. A block diagram of the video tracker is given in Figure 4.

The video tracker is operated in the centroid tracking mode. The image of the hot spot on the oil pool is selected as the target by a thresholding operation, and the tracker determines the location of the hot spot centroid within the target scene. Error signals proportional to the displacement of the target centroid from the reference position are generated.

The targeting mirror is a flat, gold-coated glass mirror 24 inches in diameter and 0.75 inches thick. It is supported by a rigid mount that allows it to be attached to the movable platform. The targeting mirror platform consists of two servo-driven rotation stages that can point the mirror within a fraction of a milliradian. The most cost effective method of assembling the platform is to use a RT 300 rotation stage and a BG 200 goniometric cradle, both from MicroControlle. The targeting mirror is mounted on the goniometric cradle, which in turn is mounted on the rotation stage. Both stages are driven by DC motors with integral tachometers and rotary encoders. The tachometers provide rate feedback to the servo controllers while the encoders indicate the angular position of the rotary stages. Limit switches are provided on both positioning stages as a safety precaution in case of control loss.

The servo controller takes the output from the video tracker and adjusts the gain and compensation for the control system. The controller is implemented in a microcomputer for flexibility in control law design. The microcomputer's digital outputs are converted into analog control signals by DACs (digital to analog converters) and fed into PWM amplifiers that drive the DC motors. In addition to handling the digital output from the video tracker, the microcomputer also accepts input from the rotary encoders and from a joystick. The former allows the angular position of the rotary stages to be displayed on the screen. This information can also be used to compute the target range if the helicopter altitude is also known. The joystick permits open loop control of the targeting

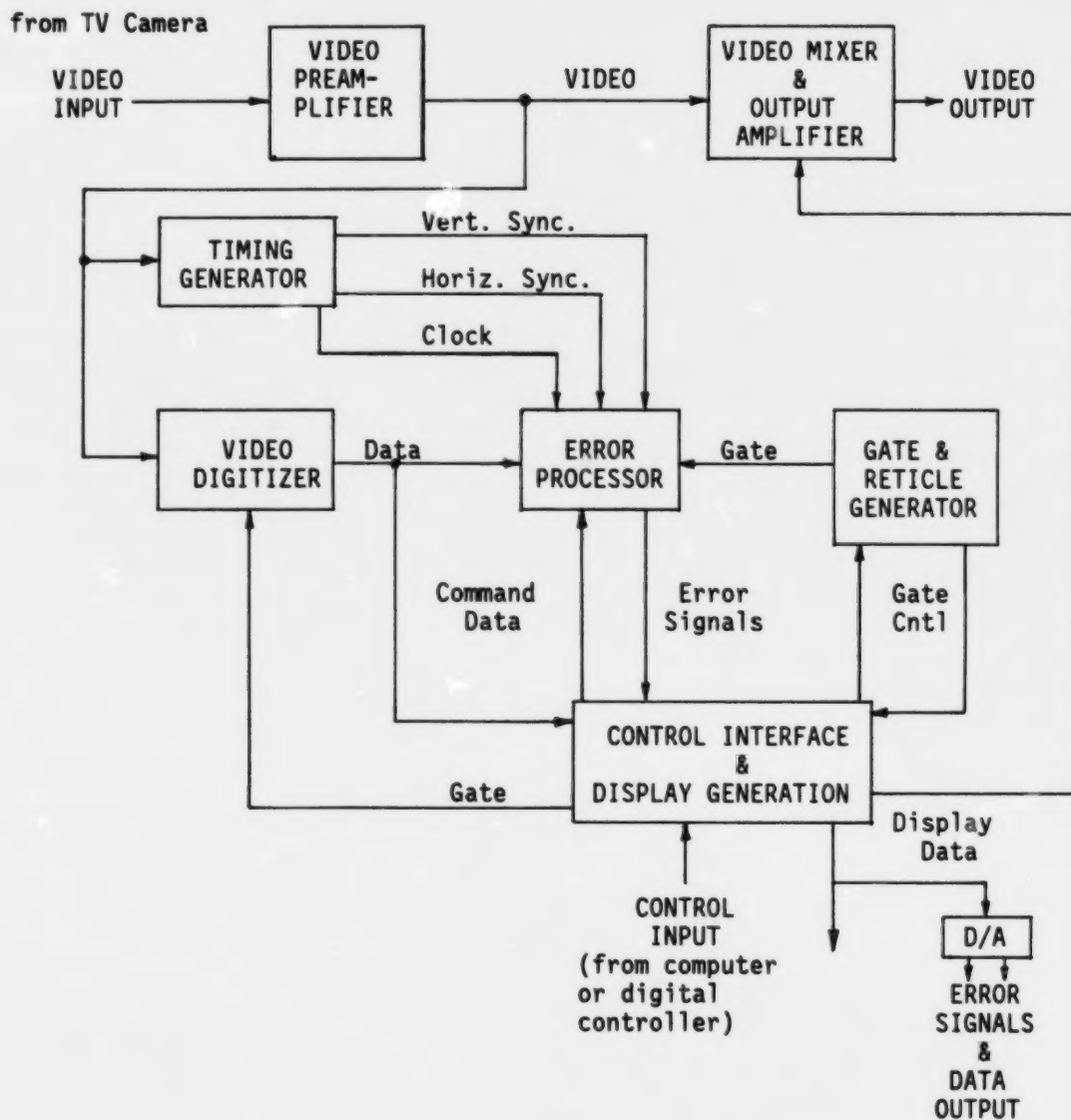


FIGURE 4 - VIDEO TRACKER BLOCK DIAGRAM

mirror position during the target acquisition phase. During this phase the video tracker's outputs are ignored by the microcomputer. Once the target has been acquired, the joystick is disabled and input is accepted from the video tracker, closing the control loop. A block diagram of the complete targeting system is shown in Figure 5. The microcomputer would also be used in the active focussing system.

Target Acquisition and Tracking

The operation of the LIOS system will be based on the following sequence of events. In the target acquisition phase, the operator locates the position on the oil pool at which the lasers are to be aimed and points the lasers at that particular spot. Since there is probably very little image contrast in the infrared prior to laser heating, a video camera is used for this task. This camera can be placed near the infrared scanner, with a dichroic beam splitter directing visible wavelengths to the camera and allowing the infrared to pass through to the scanner. The camera can be connected to the video tracker, which allows the tracking crosshairs to be superimposed on the visible image of the scene. Using the joystick controls, the operator positions the targeting mirror so that a selected point on the oil pool is centered within the field of view. The optical system is adjusted to focus the lasers, which are then turned on. An infrared image of the laser-illuminated spot appears within a second and can be used for tracking purposes.

At this point, the operator can continue to hold the lasers on target with the joystick or he can switch in the video tracker for automatic tracking. Motion of the helicopter results in a displacement of the optical field of view, and hence a displacement of the infrared image of the heated spot. Since the heated spot requires a finite amount of time to cool, it provides a thermal signature of long enough duration to allow the repositioning of the targeting mirror so that the hot spot is maintained to the center of the scene. This adjustment procedure continues until ignition of the oil is confirmed by the operator.

The LIOS system will be operated only while the helicopter is hovering to facilitate the task of keeping the laser beams on target. Using a radar altimeter for feedback, an experienced pilot can be expected to maintain a large helicopter at a desired altitude within ± 1 foot for up to a minute under normal flying conditions. The helicopter motion has a low frequency, typically less than 1 Hz, and can easily be compensated by the pointing system.

Vibration Isolation

A factor that can degrade the performance of the LIOS system is the helicopter's internal vibration, especially at the blade rotation frequency⁶. This causes jitter in the optical image, which can cause the targeting system to lose the target. Jitter is reduced by incorporating a passive vibration isolation system comprised of a

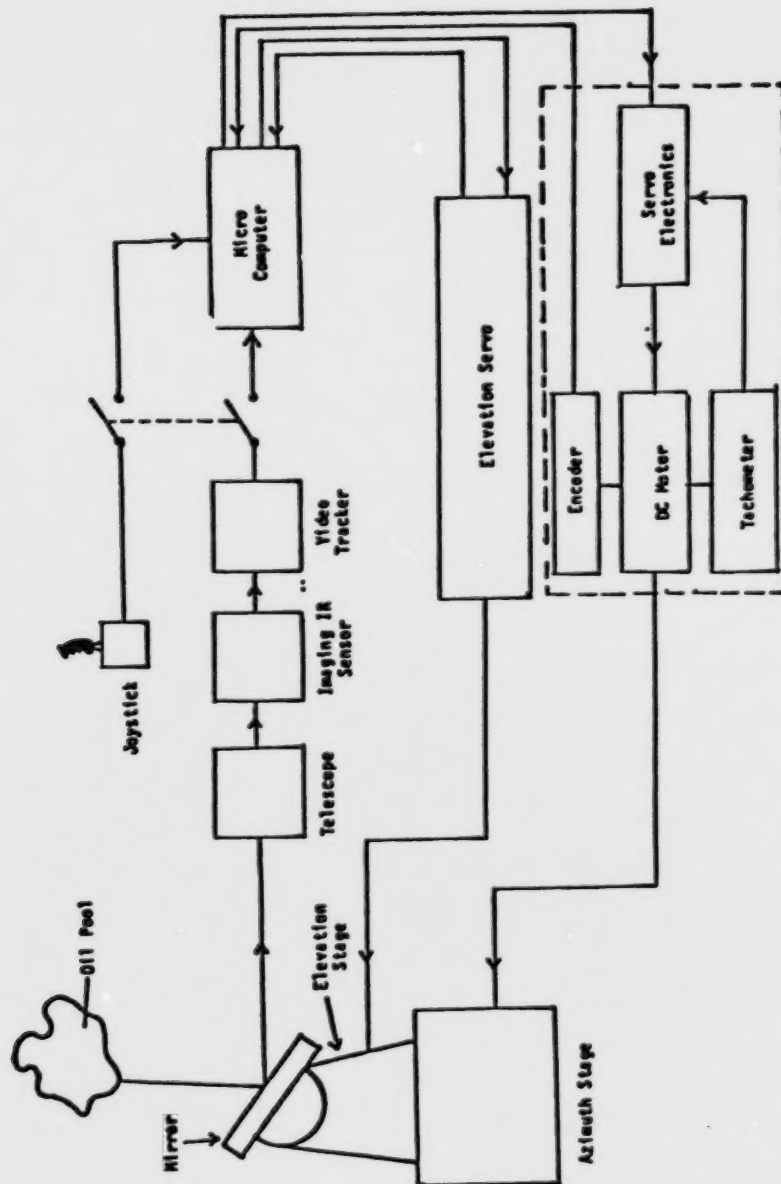


FIGURE 5 - BLOCK DIAGRAM OF L.I.O.S. TARGETING SYSTEM

number of damped springs between the optical support structure and the helicopter cabin. For example, the Sikorsky S-61 has five blades and a rotor speed of just over 3 Hz, resulting in a blade passage frequency of about 15 Hz. Thus the isolation system is designed to have a resonant frequency below 10 Hz and to attenuate at least 90% of the vibration at 15 Hz and above. Viscoelastic-spring dampers such as the Barry H64 mounts meet these specifications although their load capability is not high. Companies such as Barry Controls and Taylor Devices have the capability to custom design an isolation system to these specifications. In addition, the optical components and support structure are designed so that their resonant frequencies are much higher than the blade rotation frequency.

HELICOPTER INSTALLATION

The primary choice of helicopter for the LIOS installation is the Sikorsky S-61, chosen for its large cabin, payload capability, and availability. Although any variant of the S-61 would satisfy the demands of this installation, the HH-3F Pelicans (S-61R) of the U.S. Coast Guard became the likely choice due to their availability at this time. The S-61R features an approximately rectangular floor layout, with a length of 25 feet and a width of 6.5 feet. A 4 foot wide sliding door is located on the right side of the cabin, immediately behind the cockpit. The remaining exit is the large ramp cargo door in the rear of the helicopter. A possible layout of the LIOS system is shown in Figure 6.

Cabin Layout

As can be seen in Figure 6 the cabin of the S-61R is more than large enough for such an installation. The primary drawback in using this helicopter is the small width of the cabin door, as compared to a Bell 212 Twin Huey, for example. The width of 49" is marginally sufficient for the layout, but a wider door would be preferable. Installation of an APU and generator will be required to supply power to the CW laser, and the large cabin space in this helicopter allows for that installation with little difficulty.

One of the major requirements that had to be satisfied in this installation is the one of maintaining access to the available exits. With the 18" wide aisle between the laser installation and the cabin wall, this requirement is satisfied. The laser and flight crews are considered to be trained personnel, who are thoroughly familiar with the layout of the cabin, and its safety features. Although there are no emergency exits as such, the trained crews will not have any difficulty in evacuating the cabin in an emergency through the use of either the rear loading door, or the personnel door in the front of the cabin.

The cabin floor is rated for loads of 200 lb/ft², which is more than adequate for this installation. The optical table, focussing

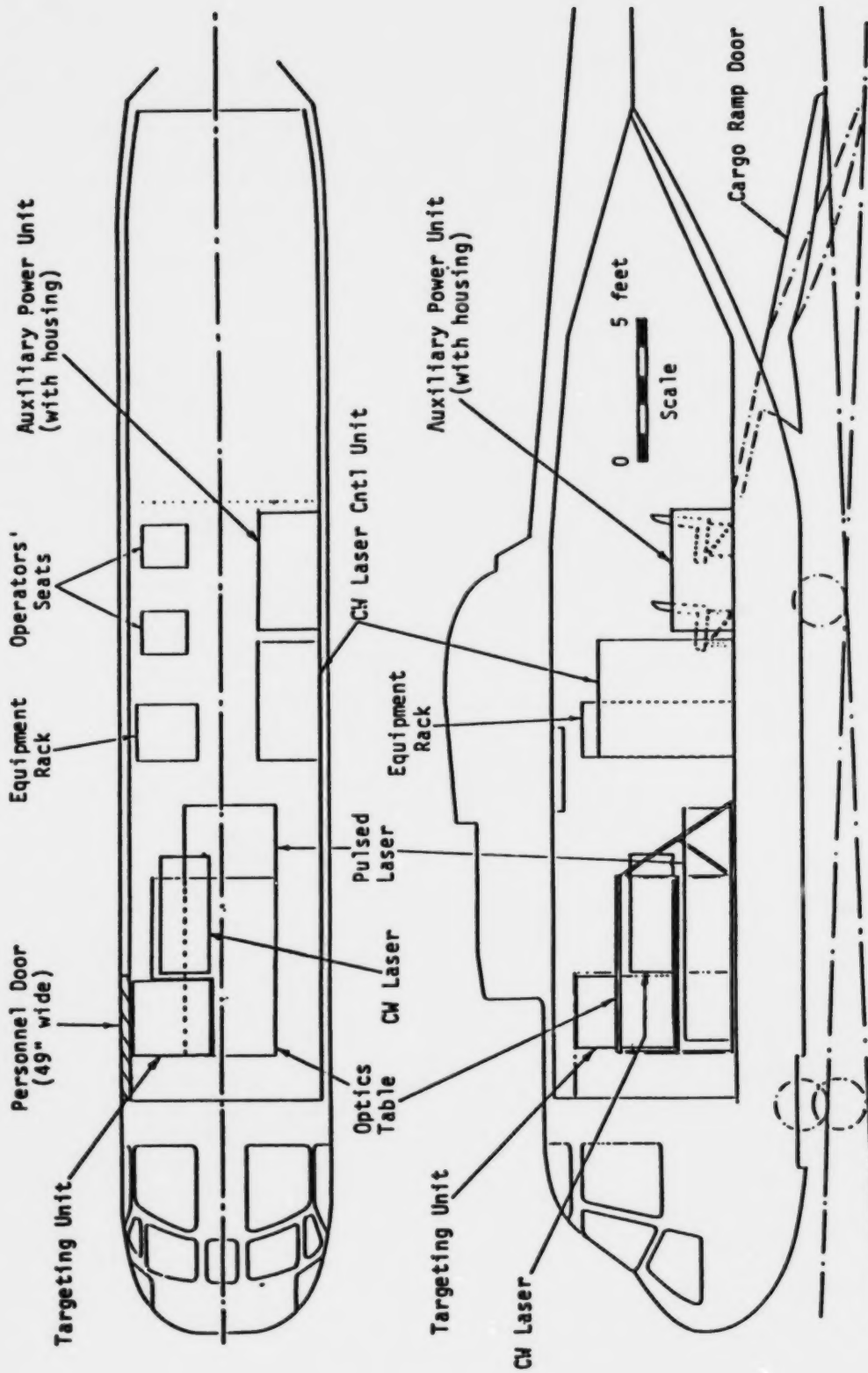


FIGURE 6 - HELICOPTER LAYOUT OF L.I.O.S. SYSTEM

optics, targeting mirror and drive, lasers, and support structure weigh about 1500 lbs. A configurational drawing of this assembly is shown in Figure 7. This assembly will be mounted on Brownline seat tracks as will the equipment rack containing the control electronics. The loaded rack is expected to weigh about 150 to 200 lbs. For ease of integration, all equipment will be packaged prior to installation in the helicopter. Structural frames will be of welded 6061-T6 aluminum construction. The laser consoles together weigh nearly 700 lbs and are situated to one side. The heat exchangers will be mounted on a separate rack and ducting will be provided to ensure a supply of cool air. Finally, the APU and generator will be installed with protective housings.

CONCLUSION

A configurational engineering design for a helicopter-based dual-laser system for igniting oil spills has been completed. The system is to be operated by trained aircraft technicians while the helicopter is hovering at an altitude of 20 m. The system incorporates a Falcon 800 CW CO₂ laser for preheating the oil and a Lumonics TEA-103 pulsed CO₂ laser for ignition. The CW laser is water-cooled using a closed system of three Lytron heat exchangers mounted in the helicopter.

An optical system incorporating a reverse Cassegrainian telescope has been designed for focussing the laser beams. Passive and active methods have been described for controlling the focussing system. The former uses a focus analyzer similar to those found in commercial zoom lens while the latter has a laser range finder. The focussing system is capable of focussing the laser beams over a range of 20 to 30 m.

The laser beams are steered and kept on target by a large mirror mounted on a two-axis mount controlled by an infrared video tracker. The tracking system uses an infrared scanning radiometer to produce a television image of the laser-heated oil spot. This image is processed by a video tracker operating in the centroid mode to generate error signals proportional to the displacement of this spot from the center of the field of view. The error voltages are amplified to drive the biaxial mirror mount. In the prototype system the video tracker can be replaced by a human operator controlling a joystick.

An auxiliary power unit must be installed on the helicopter to satisfy the power requirements of the CW laser. The helicopter installation and configurational layout of the LIOS system and the APU are now specified with costs, sizes, and weights of all system components currently identified.

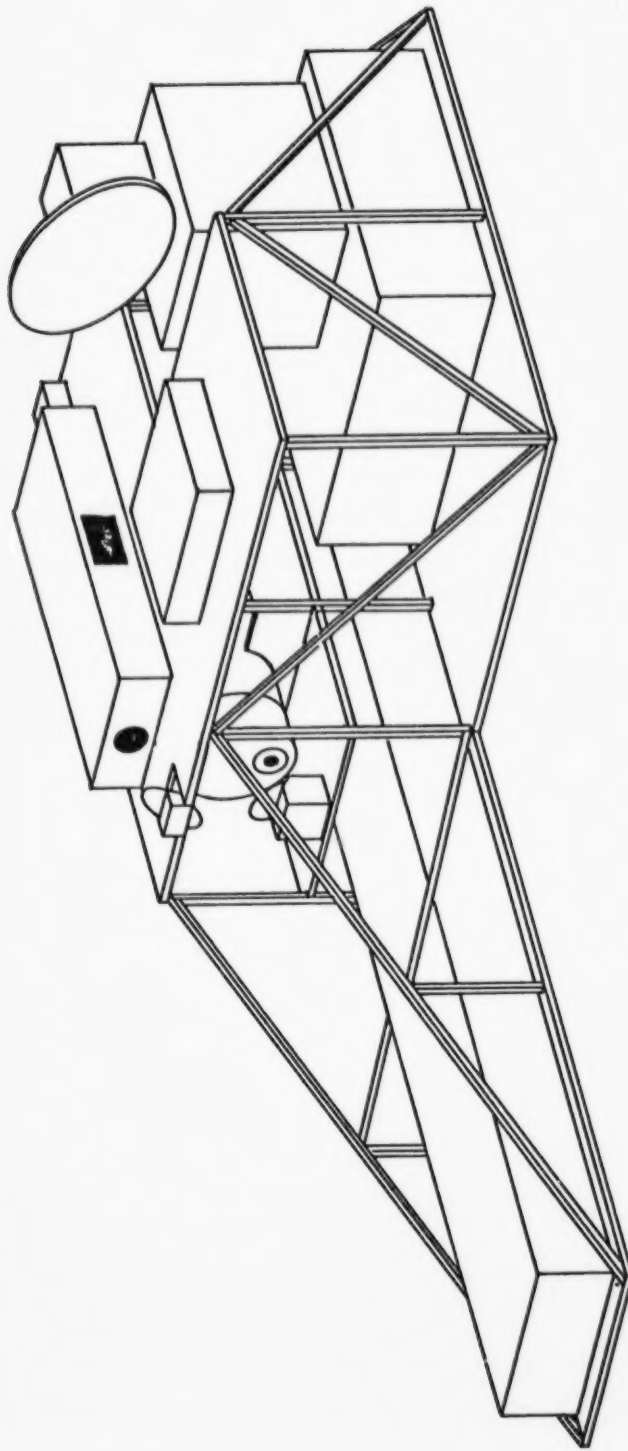


FIGURE 7 - CONFIGURATIONAL DRAWING OF L.I.O.S. SYSTEM ASSEMBLY

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COUNTERMEASURES FOR DEALING WITH SPILLS OF VISCOUS, WAXY CRUDE OILS

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INTRODUCTION

Interest in spills of highly viscous oil has increased with the recent hydrocarbon discoveries off the Newfoundland coast. The oils found to date have tended to be high in wax content and to have pour points above ambient temperature. When the oils are spilled on water they do not spread conventionally but rather convert into a semi-solid product which takes the form of mats, globules and particles. The purpose of this research study was to identify and investigate the most promising countermeasures techniques and concepts to contend with such spills. The work was funded by the Environmental Studies Revolving Fund (ESRF) programme. Mr. J. Ransom of Mobil Oil Canada, Dr. R. Goodman of Esso Resources Canada and Mr. H. Hume of Petro-Canada were ESRF scientific advisors for the study.

Study Approach

The approach used in the study involved:

1. the screening of all existing technologies, and the identification of those that appeared to be the most promising;
2. an analysis of the selected technologies to determine shortcomings with respect to viscous, waxy oils; and
3. the formulation of improvements to increase their potential effectiveness and practicability.

The study concentrated on countermeasures devices and techniques for viscous oil spills that might occur in the area of the Grand Banks. It is based on generalized predictions of the fate and behaviour of slicks of Hibernia crude oil, as described below. Although the study results have primary application to spills offshore of Newfoundland, they should nevertheless have relevance to other locations or situations where waxy, viscous oil spills may occur.

Spill Scenarios. Two east coast offshore oil spills were considered, a continuous well blowout and a large batch spill. For the well blowout it is predicted that the oil would be introduced onto the water surface in the form of droplets having diameters in the range of 1 to 5 mm. Because of the waxy nature of the oil it is postulated that these droplets would be highly viscous under most environmental conditions and would not spread or coalesce on the surface to form a conventional slick. Depending on the circumstances of the blowout these droplets would appear on the water surface downstream from a blowout

as a 'slick' that would vary in width from several hundred metres to several kilometres. As it is expected that such a 'slick' of droplets would soon diffuse and cover an area too great for effective cleanup operations, the cleanup strategy would be to contain the oil with booms at a point near the blowout site and then remove the oil with the most efficient means available. Due to the non-fluid nature of the individual droplets it is postulated that the oil would not emulsify. Nonetheless, the droplets would likely be highly viscous and non-coalescing, although they might agglomerate to form clumps. This type of oil, resulting from a subsea blowout, was named Type 1 oil for the purposes of this study.

The second type of oil is that which would result from a large batch spill. In this case, the spilled oil would be present as mats several metres wide and several centimetres thick, and globules of several millimetres or more in diameter. It is reasonable to postulate that in general the oil would undergo a significant amount of weathering before countermeasures could be implemented. It is expected that the weathering would result in the formation of a surface skin or crust that would cause the mats or globules to become non-sticky, thus preventing their recoalescing. In fact, wave energy would likely cause the mats to eventually break up to form discrete chunks of various sizes.

Laboratory Examination of Oil Properties. Because of the uncertainties regarding the exact spill properties of eastern Canadian crude oils, it was decided at the outset of the study to conduct a very brief, preliminary examination of sample oils in a small laboratory tank. Fresh Hibernia and Terra Nova crudes as well as a 15% weathered Terra Nova crude were used. These crude oils have a relatively low density (in the range of 850 to 870 kg/m³), high pour point (60°C to 250°C), and high viscosity (1500 mPa.s or greater). For the fresh (Type 1) oil, it was found that droplets would agglomerate only when physical forces were applied to accomplish this confinement. A more natural recoalescence of droplets and globules did not occur either at 30°C or 130°C. The fresh oil adhered to PVC and aluminum surfaces to a moderate extent, particularly as the plates were immersed in the oil and water (but not upon withdrawal). The fibrous surface of a polymeric sorbent pad displayed a more marked ability to absorb oil globules when placed on the water's surface.

When the weathered (Type 2) oil was discharged on water, mats and globules of oil were immediately formed. Both the globules and mats of waxy oil did not coalesce. Adhesion to PVC, metal and the sorbent pad was negligible at 30°C and only very slight at 130°C.

Environmental Conditions. In addition to the consideration of oil properties, environmental factors directly influence the selection of countermeasures systems for Grand Banks oil spills. In general, conventional offshore oil spill containment operations will only be effective during periods when wave heights are two metres or less, the wind speeds are 10 m/s (20 knots) or less, and visibility is one kilometre or greater.

Such moderate conditions persist in the Hibernia area for only brief periods. During the summer months, intervals of up to 60 hours of favourable sea conditions occur intermittently, although for about 40% of such times, visibility will be less than 1.5 km. During the other seasons, improved visibility can be expected but so can higher sea states. Booming or containment of oil spills in this environment is likely to be possible for less than one day at a time during winter months and for up to three day periods during fall or spring.

In summary, including the loss of time due to night time (50%), visibility (fog) and sea state, the estimated percentage of time during which conventional countermeasures would be applicable are summer: 20%; fall: 15%; winter: 3%; and spring: 10% (S.L. Ross 1984).

Evaluation Process. Control options were studied for their potential utility to cleanup east coast spills involving both Type 1 Oil (fresh crude droplets) and Type 2 Oil (weathered globules/mats). The alternatives considered included:

- containment
- recovery
- in-situ burning
- chemical treatment
- sinking

The evaluation process was a sequential one. An initial screening step was first conducted to reject systems that were obviously inappropriate. Reasons for early rejection of a technique related mainly to limitations with respect to the specific oil properties. This was followed by a further examination of the screened information in a brainstorming type of exercise. Brainstorming was carried out with an initial consideration of existing (i.e., known) devices/concepts which are applicable as is or with possible modifications. This approach was felt to be justified since existing devices/concepts could be more accurately evaluated, and since modifying an existing device would afford a greater probability of ultimate success than starting with a new concept. With this rationale in mind the brainstorming team was first asked to consider promising existing devices, then to consider upgrading modifications if required, and finally, if these two methods failed to provide a satisfactory solution, to suggest totally new ideas.

EVALUATION RESULTS

The detailed evaluation results, including brainstormed concepts and ideas which were rejected can be found in the complete report of this study (S.L. Ross 1986). In the following sections, only the most promising techniques are discussed.

Containment

The control and containment of offshore spills is determined by environmental conditions rather than oil properties. Although favourable conditions are infrequent off the east coast of Canada, they do exist for short periods lasting a few days or less at a time. Quick deployment and retrieval capabilities are therefore priority features to be incorporated in an offshore boom. Durability of construction and general robustness would also be essential characteristics since the frequency of handling is relatively high. High reserve buoyancy and good wave response would also be important to the adequate performance of an offshore boom. Since Type 2 oil does not adhere to surfaces, there is less of a concern about choice of material.

These criteria are met to some degree by the Vikoma Boom Deck Reel, Nordan Oil Boom, Roulunds Ro-Boom, and Kepner Sea-Curtain, each of which is analysed in the study report (S.L. Ross 1986).

Another approach to containment that was reviewed was the Jackson/West Net System. It offers both fast deployment and retrieval using techniques similar to purse seining, and has been proposed for both the confinement and collection of oil. While the fine mesh net might not yield significant oil losses, some oil might escape through the net as a sheen. Of greater concern is the structural integrity and vertical stability of the West Net if used as an offshore boom. Recent design changes have resulted in the use of vertical nylon stiffeners, prestretched rope tension members, expanded PVC floats, and an improved fabric weave. All of the above are expected to improve the boom's durability but this is currently unproved.

In summary, four products which are all currently available were identified as being acceptable for offshore containment. Although some time was devoted to containment techniques in the brainstorming phase, no modifications or new ideas were identified that would provide an improved capability.

Preliminary Screening of Recovery Devices

Due to the preponderance of existing oil spill recovery devices and techniques, an initial screening was first carried out to eliminate those which were thought to be obviously inappropriate. Application to Type 1 and Type 2 oils was considered separately.

The recovery techniques were considered under the generic groups of:

- weirs
- oleophilic surface devices
- mechanical devices
- suction devices
- hydrodynamic devices

The screening was based mainly on the ability of each technique to process the oil of interest (i.e., Type 1 or Type 2). As well, a recovery rate less than 50 m³/hr was cause for rejection, although if this was the sole drawback, the technique was considered for nearshore operations.

The techniques found worthy of further consideration can be summarized as follows:

- Type 1 Oil
 - weir devices
 - oleophilic surface devices, especially fibrous belts
 - mechanical devices, specifically non-oleophilic rotating belt
 - hydrodynamic devices
- Type 2 Oil
 - mechanical devices, specifically the Seawolf toothed disc and Shark 5000 skimmers
 - hydrodynamic devices for weathered particles only

Several important problems that apply to all the any collection devices were noted:

- Type 1 Oil
 - possible agglomeration of oil particles, causing clogging of recovery components, pump suctions etc.
 - oil is somewhat adhesive, a possible detriment to weir and hydrodynamic devices
- Type 2 Oil
 - extremely poor flow characteristics of the viscous mats requires that any skimmer must have some sort of feeding mechanism
 - transfer mechanisms must be able to deal with viscous mats and chunks

This preliminary evaluation was used as the basis for further consideration in the succeeding phases of the study.

Recovery Devices for Type 1 Oil

As a result of the screening process, four generic recovery devices were identified as having promise. Of those four, hydrodynamic devices were felt to offer the greatest potential.

Hydrodynamic Devices. One specific hydrodynamic device, the Walosep skimmer, is selected for discussion here although the comments provided could be generally applied to other devices that use the same principle of operation. The Walosep was focused on due to encouraging test tank results (Smith and Lichte 1981) and its commercial availability.

The Walosep is shown schematically in Figure 1. Its principle of operation is the use of submerged rotating vanes which develop a flow of the surface layer into the device. In the collection chamber, water flows through openings in the bottom of the chamber, while the buoyant oil is concentrated in the centre. From this central concentrated area the oil is pumped off by a remote diaphragm pump.

It is expected that the flow through effect created by the rotating vanes would successfully entrain a stream of Type 1 oil particles. The capability of the skimmer has been proved in test tank trials with both light and heavy oils, and was found to be fairly insensitive to waves up to 0.5 m in height. Recovery rates in these trials were in the range of 50 to 100 m³/hr.

Several possible drawbacks were noted. The somewhat sticky and viscous nature of Type 1 oil particles could lead to problems with the oil adhering to the collection chamber and other surfaces. As well, the possible agglomeration of these particles could clog the inlet zone. It is expected that the flow-through effect would eliminate such clogging problems, but testing should be done to confirm this. The adhesion problem could be reduced through the use of surface coatings (such as teflon) or by heating the offending surfaces.

A more serious drawback is the lack of a positive suction feed at the point of oil removal (as indicated on Figure 1). With flowing oils, a positive head is developed within the stator; this head forces oil into the collection pipe allowing the oil to be removed by a remote diaphragm pump. It is not certain whether a slurry of Type 1 particles would flow into the collection pipe in the same manner, and whether a remotely located diaphragm pump could maintain the required suction head. It may be necessary to provide a suction feeding device within the stator. An example of such a modification proposed by the study team is the use of an auger to feed the collection pipe (Figure 2).

In summary, the Walosep skimmer should have great potential for the recovery of Type 1 oil in an offshore environment, and with a smaller sized unit, for nearshore operations as well. Possible problems with oil adhering to and clogging the surfaces of the collection chamber, and with feeding the collection pipe appear to be solvable.

Other Devices. The remaining three types of devices were considered to have less potential for offshore operations.

A rotating non-oleophilic belt skimmer such as the JBF DIP would be applicable to Type 1 oils, although its sensitivity to waves makes it less desirable in the offshore. Certain oleophilic devices, such as those employing a fibrous belt, could recover Type 1 oil; however, their generally low recovery rates and poor wave response of the required working platform renders them less applicable to offshore operations. Weir devices were considered due to their simplicity and the ease of oil/water separation for the oils of interest; however, the agglomeration and clumping of Type 1 droplets would limit the flow of oil over a weir lip and would negate their practicality.

Recovery Devices for Type 2 Oil

As a result of the screening process, three recovery devices were identified as having promise with Type 2 oil. One new idea was also developed in the brainstorming process. Of these four, the toothed disc skimmer and Shark 5000 were considered to be the most promising.

Toothed Disc Skimmer. The toothed disc skimmer, shown in Figure 3, was developed by the British Petroleum Company and is presently marketed by Vikoma International. Its

FIGURE 2 : WALOSEP SKIMMER
USE OF AUGER
TO FEED DISCHARGE HOSE

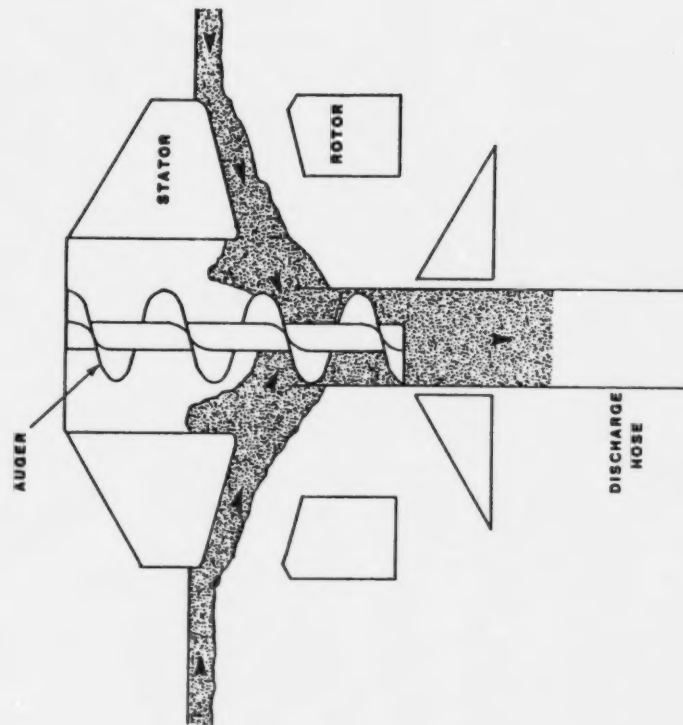


FIGURE 1 : WALOSEP SKIMMER
PRINCIPLE OF OPERATION

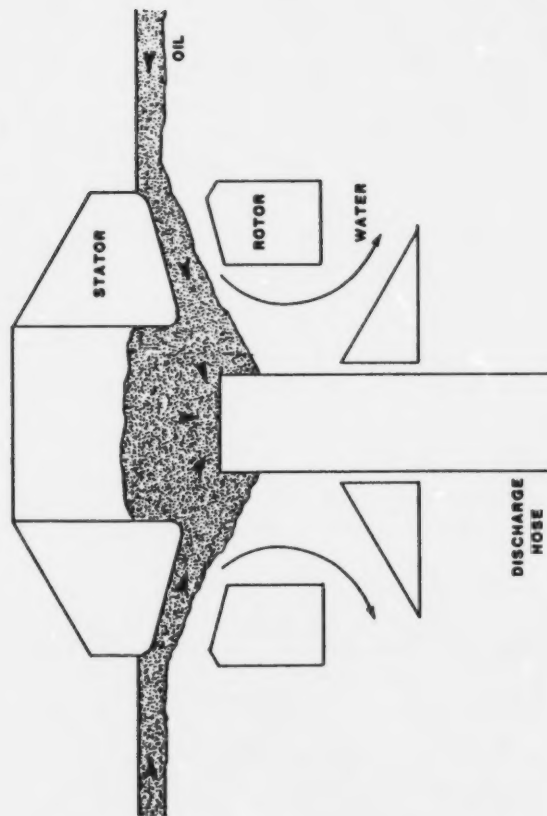


FIGURE 3 : TOOTHED DISC SKIMMER
PRINCIPLE OF OPERATION

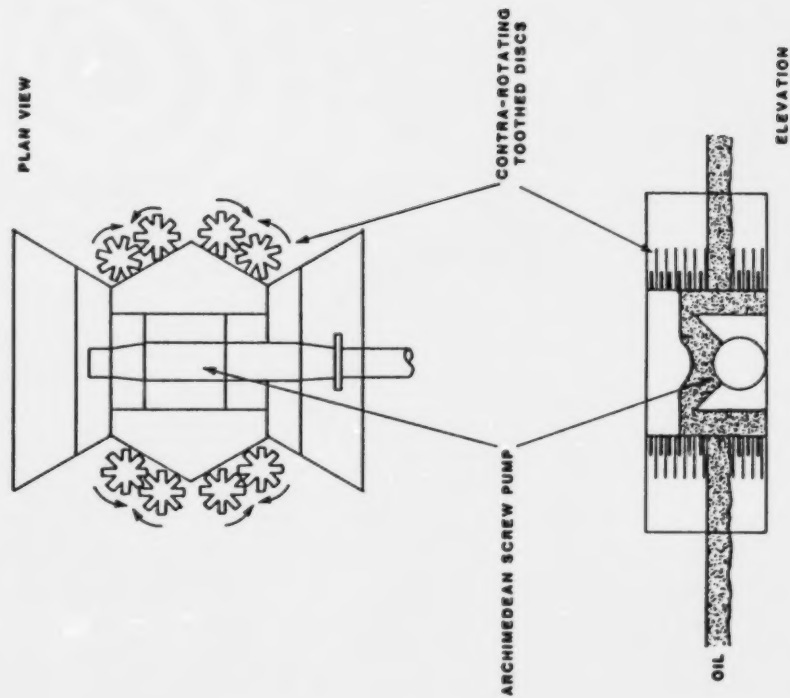
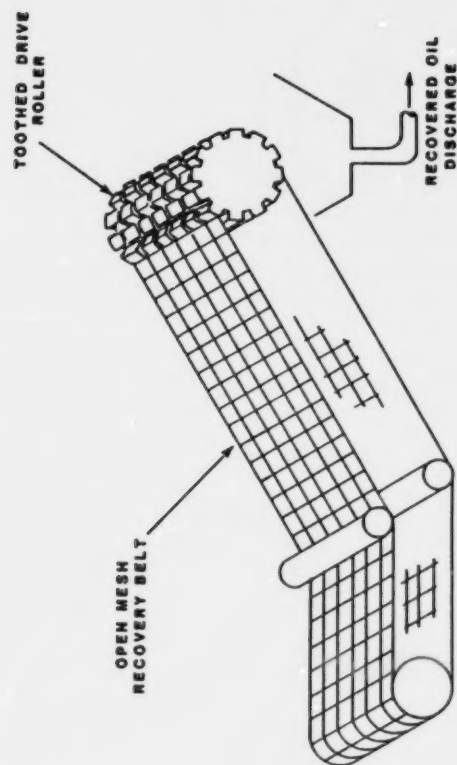


FIGURE 4 : SHARK 5000 SKIMMER
PRINCIPLE OF OPERATION



principle of operation is the use of two vertical arrays of intermeshing toothed discs which draw in oil, and push the oil into a collection chamber from where it is pumped off by a screw pump. The pressure head created in the collection tube minimizes the amount of free water collected.

The vertical orientation of the disc arrays has the advantage of not requiring precise positioning at the oil/water interface, and enables the mechanism to work continuously, even when subjected to wave motion. The disc's teeth would pierce the mats and chunks of Type 2 oil, and effectively draw in a cohesive oil mass.

The main drawback associated with the toothed disc is its low recovery rate. Preliminary tests (Scott 1983) with the device indicated a maximum recovery rate in the range of 5 m³/hr per pair of disc banks. A conceptual design incorporating four pairs of disc banks has been developed, but even its rate of 20 m³/hr is not sufficient for an effective offshore recovery operation. However, its proved capability of handling very viscous oils makes it ideally suited to smaller scale nearshore operations.

Shark 5000 Skimmer. The Shark 5000 Heavy Oil Recovery Unit, shown in Figure 4, is produced and marketed by Oil Recovery International. The general concept is similar to that of other rotating oleophilic belt skimmers, but it has two key improvements which allow it to cope with very viscous oils. The improvements are the use of an open-mesh, chain link recovery belt to collect oil from the water surface, and a toothed drive roller to forcibly eject the collected oil from the belt.

The Shark 5000 was designed specifically for use in harbours, lagoons, and other calm water environments; the oil recovery mechanism must be accurately located at the water surface, and would be adversely affected by wave motion of 100 mm or greater. As such it is a poor candidate for offshore recovery operations. During field tests (Thomas 1982) of the device in a calm environment, its recovery capability was proved with a variety of viscous oils, including a fuel oil emulsion and Beatrice crude oil, a waxy North Sea crude with properties similar to the specified Type 2 oil. A maximum recovery rate of approximately 20 m³/hr was obtained in these trials.

Netting Systems. The use of porous nets has been proposed for the containment and possible recovery of highly viscous oils. Several systems have been evaluated (Thomas and Morris 1983, Suzuki 1985, and Gill 1985), using nets with a pore size of approximately 1 mm. Such nets are able to contain viscous, non-flowing oils under normal sea conditions.

The reasons for considering the use of nets are:

- compared with conventional boom materials, the porous material provides less resistance to sea forces; hence greater boom lengths can be used;
- the boom is easily deployed and retrieved, and is compact when stored, allowing small fishing boats to use it; and
- as with the purse-seining of fish, the net surrounding an oil slick can be drawn in, thus thickening the oil for the subsequent use of oil recovery devices.

The main disadvantage of a netting system is that it is essentially a batch system: in an offshore situation, its 'recovery' rate is not likely to be great enough for an effective response.

For nearshore situations, a possible mode of operation using nets is to capture oil slicks, then recover the nets with a trawler type vessel. Although it has been found that lifting the net and its contained oil out of the water results in excessive oil losses by extrusion through the mesh, it may be possible to drag the net and its oil up the ramp of a stern trawler.

Three other possible methods were proposed for the use of nets. The first is to tow the contained oil to shore at high tide; when the tide falls and the 'package' is on dry land, the net and oil can be removed with loaders and dumptrucks. This method has been used successfully during the Patmos spill in Italy, March 1985. It may not prove to be practical in the area of interest because of lack of access, and abrasion and tearing of the net on rocky beaches. A second proposed idea was to provide a strip (say 30 cm wide) of normal boom material along the bottom of the net boom; as the net is drawn in this strip would provide an impervious barrier to prevent or limit extrusion losses as the net is lifted out of the water.

A third idea for the use of nets relates specifically to subsea blowouts; it was suggested that a piece of netting suspended over the blowout plume could divert oil from the plume to a collection point. The major unknown with this idea is the ability of the net to selectively divert oil particles in the presence of gas.

Other Devices. Two other mechanical devices were considered for Type 2 oil: a paddle wheel device, similar to the Clowsor Paddle Wheel Skimmer, and a bucket conveyor system. Both were rejected for offshore use but were considered to have application to nearshore spills.

In-Situ Burning

As there have been no burning experiments done with viscous, waxy crudes, the potential of in-situ burning was evaluated on the basis of previous experience on the in-situ burning of conventional crudes and on the oil property assumptions stated previously.

For Type 1 and Type 2 oils, it is expected that the oil can be contained for burning, although the environmental limitations are similar to those for conventional booming operations. Specifically, favourable sea and weather conditions exist only 3% of the time in winter and 20% of the time in summer. Further complicating the use of in-situ burning is the fact that currently available fireproof booms are heavy and cumbersome, and thus not easily deployed and retrieved. This is a serious drawback considering the short duration of favourable conditions, following which the boom would have to be retrieved. New, lightweight fireproof booms that are now becoming available could overcome this limitation although these may suffer from a lower durability potential.

With respect to the burning properties of waxy crudes, it is expected that both Type 1 and Type 2 oils will burn once ignited.

For Type 1 oil it is expected that the heat from the fire will continually "melt" surrounding droplets, allowing them to flow into the fire zone, thus sustaining the burn. It may be necessary to promote initial ignition with diesel fuel to ensure an adequate initial heat source. Further testing is required to determine the limiting parameters.

For Type 2 oil, mats and chunks, it is expected that ignition and subsequent combustion would be comparable to that of conventional crudes. In fact, the non-spreading nature of these oils may allow removal efficiencies greater than that of conventional oils.

Chemical Treatment

It is known that chemical dispersants are not effective on viscous oil spills. Oil viscosities of about 2000 mPa.s are believed to be the upper limit (ITOPF 1982). It is likely, then, that the conventional use of dispersants will not work on Type 1 or Type 2 oils. That is, dispersants will not be effective on surface concentrations of waxy crude oil when the pour point of the oil is significantly greater than ambient temperatures, say, 10 degrees C higher (Martinelli and Lynch 1980).

It is conceivable that dispersants can be effective on a waxy crude oil spill when the oil temperature is higher than its pour point, that is, when they are still relatively non-viscous. This circumstance exists in oil well blowouts when the hot oil has yet to enter the relatively cold environment or when the hot oil enters the water environment (for subsea blowouts) but has not yet cooled to a temperature below its pour point. These situations are different and are discussed separately.

Injecting Dispersant into the BOP Stack. Oil flowing through the BOP stack in an oil well blowout is hot and thus non-viscous. If dispersants could be injected into this oil prior to its entering the water, it is possible that the dispersant would mix with the oil. Quick dispersion of the oil once it enters the water phase would be inevitable if good dispersant/oil mixing occurred in the pipe. A recent, brief study of the concept (Westergaard 1985) concluded that the technique presents no engineering problems in terms of using either existing choke and kill lines on a BOP or a purpose-built access port and line. Research would be required to determine if the oil would indeed mix well with the injected dispersant considering the two-phase nature of the flow (oil and gas) and the short mixing time available.

One serious drawback with the approach is that it might be seen as interference by those attempting to work on the same BOP stack to bring the blowout under control, an activity which obviously would take precedence over spill cleanup. If both operations could not be accomplished simultaneously or cooperatively, then the spill countermeasures approach could become a two-phased one: One could first attempt to inject and mix dispersant into the oil plume immediately above the discharge point and away from the BOP stack; if attempts at blowout control at the well-head failed, then the use of the BOP lines to inject dispersant could proceed.

Injecting Dispersant into the Oil Plume in Water. Hot oil discharging from a sub-sea blowout into the water would cool quickly but if dispersants could somehow be added to the discharging oil prior to its reaching environmental temperatures, dispersion could be effected. The main concern related to this idea is that major losses of dispersant to the water phase could occur. Thus, to be feasible the approach would require the use of highly oleophilic dispersants or so-called emulsion inhibitors (Ross et al 1985), and the use of a mixing system to ensure good oil/dispersant contact. One such mixing device could be a short "chimney" positioned over the well in which baffles or other mixing aids operated.

Sinkants

Given the constraints on conventional recovery operations imposed by the harsh environment, consideration was given to the application of sinking agents. Such agents, when applied to a floating oil slick, could sink the slick and limit the areal extent of environmental damages. This technique has several advantages, including the fact that it does not require sophisticated and wave-sensitive application equipment and that it offers the possibility for a high rate, single step disposal process. Environmentally, the main disadvantages are that the oil is sunk to the bottom in its most toxic (unweathered) form and once there, biodegrades at a low rate.

There are several negative aspects that specifically relate to the properties of viscous, waxy crude oils. The first is the possibility that, after even slight weathering, the surface of the oil chunks or particles will be non-sticky and therefore not amenable to sinkant application. Secondly, the oils of interest are of relatively low density and therefore, are generally more difficult to sink.

For these reasons, the use of sinking agents was not seen to be a viable alternative. Should an agent be found to be effective (i.e., a 'sticky' agent) with viscous, waxy crudes other factors which will require consideration (and which might limit their attractiveness) include sinkant delivery, application operations, and other logistical requirements.

CONCLUSIONS AND RECOMMENDATIONS

An evaluation of existing and proposed countermeasures devices, and a brainstorming of possible improvements have led to the following conclusions and recommendations.

Conclusions

1. For the purposes of this study, two categories for the properties of viscous, waxy crude oils were defined:
 - Type 1, fresh oil that floats as individual, relatively small (1-5 mm) droplets. These droplets may agglomerate but will not recombine, and 'slicks' will comprise droplets and clumps; and
 - Type 2, weathered oil that forms globules and mats. These oil masses are not likely to coalesce or agglomerate, nor will they cling or adhere to oleophilic surfaces. Globules could be millimetres to centimetres in diameter, and mats could be up to several centimetres in thickness.
2. The effective skimming of viscous, waxy oil spills (or other types of oil spills) is dependent on the ability to contain and concentrate the oil. The main criterion for the selection of containment devices is the short periods of acceptable working conditions that are characteristic of the Grand Banks where waxy crudes have been discovered. As such, desirable booms are those that are robust and easily deployed and retrieved, booms such as the Nordan and Kepner Sea Curtain, both of which are stored on reel-packs. The Roulunds Ro-Boom and Vikoma Ocean Pack are other acceptable alternatives.
3. For inshore containment, netting systems such as the Jackson/West Net may be useful. Small vessels, each handling up to 1 km of boom, could be used to encircle and concentrate oil in a batch-type process.
4. Of the recovery devices considered for Type 1 oil, hydrodynamic devices - specifically the Mattsson Walosep skimmer - were felt to offer the best prospects for offshore oil recovery. Several specific problems were noted with the device, namely, possible adhesion of oil to the vanes and collection chamber and lack of a positive suction feed at the collection pipe inlet. It was felt that these problems could be overcome with further research and equipment modifications. Other devices considered for offshore Type 1 oil spills were deemed unacceptable due to inapplicability vis-a-vis the specific oil properties, or limitations with regards to oil recovery rate and/or environmental conditions. It is proposed that the nearshore recovery of Type 1 oil could be effected with a down-sized hydrodynamic device, or with a mechanical device such as a rotating non-oleophilic belt (i.e., a device similar to the JBF DIP). Although the latter is not recommended for offshore use because of its low recovery rates and sensitivity to waves, these factors are less critical in a nearshore operation.
5. For the recovery of Type 2 oil, no techniques were judged to be applicable to offshore recovery. Although several techniques were determined to be applicable to the specific oil properties, each had severe limitations with respect to achievable recovery rates and/or sensitivity to waves.

Three techniques were noted for nearshore recovery operations: the toothed disc and Shark 5000 skimmers, and the use of porous nets for containing and concentrating nearshore slicks.

6. Conventional chemical dispersion is not applicable due to the high viscosity of the subject oil. The only possibility for using dispersants is to apply them when the oil is fresh and not yet cooled to ambient temperatures. This might be accomplished by injecting the dispersants into or near the well-head of a blowing well, a concept which is currently unattractive, but may be refined through further research.
7. In-situ burning is an attractive countermeasures option; however, it requires containment of the oil slick and, therefore, its applicability would be subject to the environmental limitations of booming operations.
8. The use of sinking agents is not applicable due to the poor adhesive properties of the subject oil, and the known problems of sinking a high viscosity, low density oil.

Recommendations

1. Further study is required to elucidate the spill related properties of waxy crude oils, especially on the questions of droplet formation, droplet agglomeration, droplet re-coalescence, adherence properties, skin or crust formation, and emulsion tendencies.*
2. Field tests of the Walosep skimmer with Type 1 oil would be useful to confirm the assumptions made in the evaluation process. Upgrading modifications are recommended in the form of surface coatings or the use of heat to prevent oil adhering to the vanes and collection chamber, and in the use of a vertically oriented screw-auger to provide a positive suction feed at the collection pipe inlet.
3. Field tests of the Seawolf toothed disc and Shark 5000 skimmers with Type 2 oil would be useful to confirm their applicability to the specific oils of interest.
4. The concept of injecting dispersants into or near the well-head of subsea blowouts warrants further research to determine its logistical limitations, possible effectiveness, and technical feasibility.
5. Further research is required on the burning of Type 1 droplets, and to determine the limiting parameters of burning both types of oil.

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IN-SITU COMBUSTION OF STRANDED OIL ON REMOTE SHORELINES

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INTRODUCTION

Oiling of shorelines by accidental oil spills is a continuing problem. Any oil that comes in contact with a shoreline has the potential for adversely affecting biological and physical processes. For this reason, various clean-up techniques have been developed to mitigate the environmental damages that follow a spill event. In some cases, however, the clean-up techniques result in impacts of their own and, particularly if carelessly implemented, can result in greater ecological, recreational, and economic damage than the oil contamination itself.

Background

The type of coastal environment will determine to a large extent the degree of oil degradation and dispersion. Clean-up methods employed to remove the beached oil will, to a large extent, be influenced by the type of coastal environment as well as by the adverse working conditions which are likely to be encountered on remote shorelines.

Before the actual contamination of the shoreline, the oil slick will undergo a series of physical changes including emulsification, evaporation, elution, biodegradation, and chemical oxidation. Beached oils will be mainly subject to evaporation and emulsification. Because of the effects of the various physical changes of the oil slick, the viscosity of the oil will increase, subsequently making in-situ combustion of the oil easier. This is due to smaller penetration of the oil into the beach substrate and a thicker oil layer on the beach surface.

Factors Affecting Stranded Oils

The penetration depth of an oil slick landing on a beach will vary as to the granular size of the beach sediment. The finer grained sediments allow less penetration than the coarse grained ones, such as gravel. Also, the viscosity of the oil will determine the penetration depth, which increases as the oil viscosity decreases.

In general, the thickness of oiled sediment increases with the age of the spill and the grain size. Lower viscosity oils, (recently spilled) stranded on a large grain sized beach will create a thick oil sediment. Thus, removal is more difficult on coarse-sand and gravel beaches, than on fine-sand or silt beaches.

Existing Beach Clean-up Methods

Twenty-three shoreline clean-up techniques have been identified as being in general use. Selection of the proper technique to clean an oil-contaminated shoreline depends on:

- 1) Type of substrate.
- 2) amount of oil contamination.
- 3) depth of oil contamination.
- 4) type of oil contamination.
- 5) type of oil.

- 6) trafficability of equipment on the shoreline, and
- 7) environmental sensitivity of the contaminated shoreline.

The majority of the beach clean-up techniques currently used today involves a disturbance of the top critical 3 to 10 cm of beach substrate.

This disturbance is accomplished by either scraping away the top substrate with motorized graders, or in the case of a remote inaccessible shoreline, manual removal. Hydraulic flushing, another popular method, presents a threat of recontamination of unaffected areas if run-off from the flushing operation is not properly channeled and collected.

Physical Effects

The major physical impact associated with shoreline clean-up usually results from sediment removal. The removal of large quantities of sediment may upset the littoral sediment balance.

The biological effects of sediment removal are heavily dependent on the depth and, to a lesser degree, area of substrate removed regardless of the clean-up technique used or sediment type. In general, the number and diversity of affected organisms and habitats increases as the depth of removed substrate increases.

In-situ cleaning of oil-contaminated sediments usually does not cause severe physical impacts upon a shoreline. It also eliminates recontamination by oil that is removed but not effectively recovered and substrate disturbance caused by extensive manual labour.

With regards to the previous criteria, in-situ combustion of oil spills on remote shorelines is considered to be the most promising clean-up and disposal method.

PRESENT METHOD OF IN-SITU COMBUSTION

The advantages of in-situ combustion includes:

- 1) Speed - A burn can be initiated and completed within a relatively short time.
- 2) Economy - The small requirement for equipment and manpower, placing in-situ combustion among the most economical.
- 3) Ecology - There is little evidence that burning has a harmful effect on the biological balance of the shoreline. One drawback is air pollution.
- 4) Toxicity - Combustion can be accomplished without the addition of toxic or polluting materials.

Main Problems

The main problems with in-situ combustion are of achieving ignition and maintaining combustion, which in many cases ceases with the removal of the heat source.

This is most likely to happen with:

- 1) small oil thicknesses,
- 2) aged oil,
- 3) high water concentration, and
- 4) high wind velocities.

In response to the above criteria and for a more effective beach clean-up technique, Bennett Environmental Consultants Ltd. is currently completing a study financed by the Environmental Studies Revolving Fund, (ESRF).

BEACH BURNER CONCEPT

Bennett Environmental Consultants Ltd. in reaction to the problem of cleaning material removed from beaches has in the recent past designed and tested a road transportable rotary incinerator. Based on this experience, it was apparent that incineration was the most effective oil spill disposal tool.

The Bennett Beach Burner is an open bottomed combustion chamber fitted with skirts. The energy of the burner it incorporates is effectively retained inside the combustion chamber ensuring that this energy is delivered to the beach target area.

The combustion chamber is sized to provide an adequate dwell time for the vaporized gases to complete their oxidation thereby minimizing smoke emissions.

As the study is at Phase I of a three phase proposal, this paper addresses the feasibility of the concept.

The feasibility was tested and results quantified to establish a relative cost as opposed to other methods. The tests included different types of beaches, oil types and operating conditions.

Equipment Design and Selection

To establish a starting point, a theoretical heat balance was developed on computer, relating oil thickness, percentage of oil, combustion chamber volume, and the theoretical advance rate. With this data tabulated, a prototype Mk I Model was designed as per diagram 1.

The obvious fuel to use was oil, preferably diesel fuel, due to its wide availability and probable compatibility with other mechanical support equipment. As the theoretical sizing had been done on a 630,000 KJ basis, a packaged fuel oil burner, capable of running on diesel fuel was found. A unit of this type comes complete with fuel pump, combustion air blower, and a continuous spark ignition system. Since it handles a liquid fuel, flame safety equipment was not required and as a consequence its electric power supply requirements are less rigorous than those of the equivalent gas burner. Some aspects of these burners, while not immediately apparent through lack of information, were found to be very beneficial. In particular, the quantity and method of fuel supply was found to be adjustable by changing the burner nozzle size.

To provide combustion air for the spilled oil, it was proposed to introduce secondary air at a location considered to be downstream of the ignition burner and beach flame impingement area.

Weight being a criteria of the final unit, it was proposed to use flexible refractory material rather than castable. The material selected was "Cerwool", which is secured in place by mechanical fasteners welded to the inside walls of the combustion chamber base.

The remaining area of material selection was skirting. A material called "Siltemp" was selected being very flexible and light in weight.

The construction of the burner was of mild steel as the prototype, in its wheeled configuration, was not weight sensitive.

The equipment was also provided with an array of temperature sensors, and fuel flow meters.

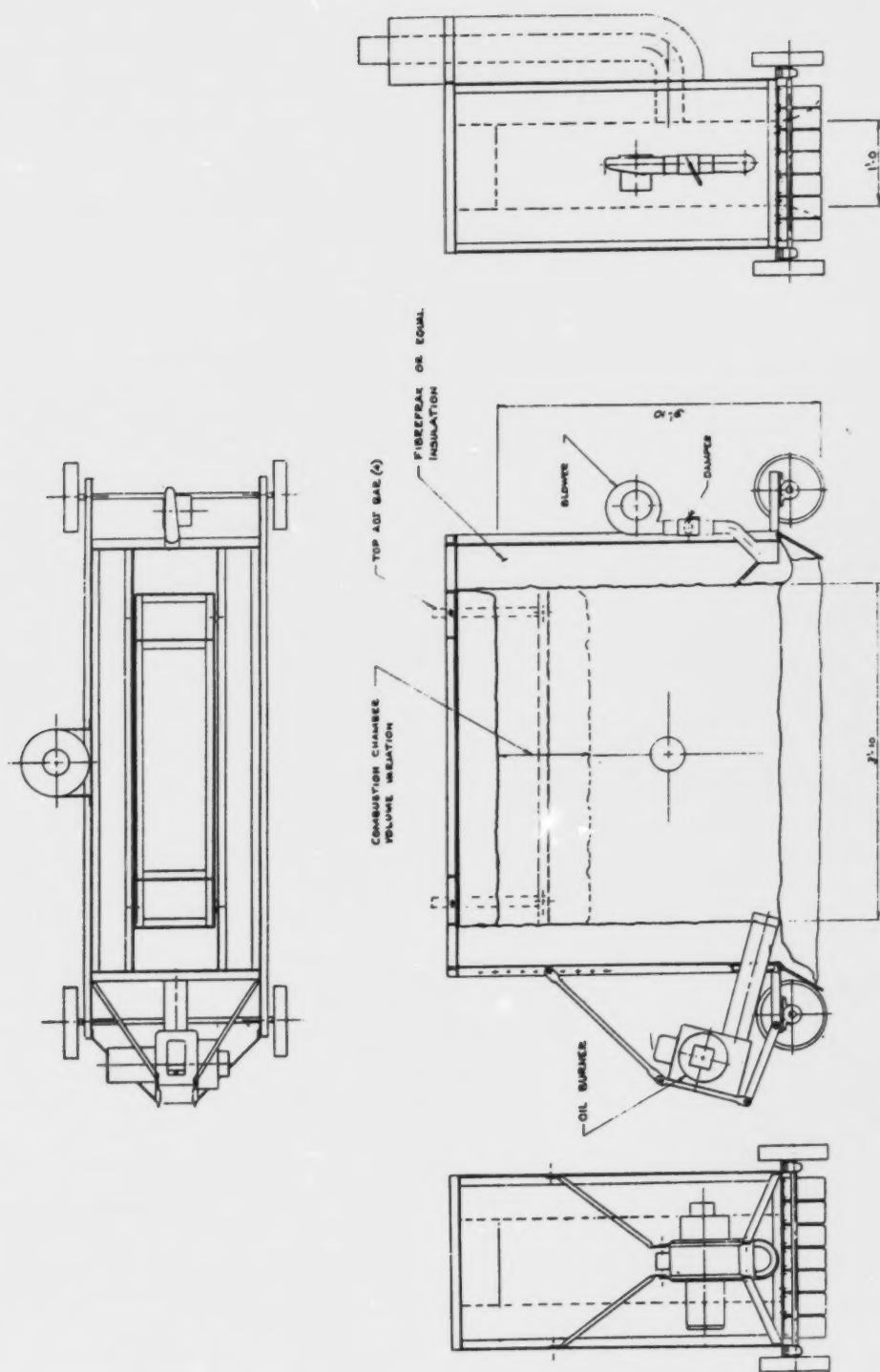


FIGURE I
General Arrangement Of Test Burner

Equipment Specifications

Combustion Chamber Volume	405 cu m
Combustion Chamber Temperature - inner	1000 C
- outer	200 C
Oil Thickness Range	0.38 - 1.10 mm
Energy Supplied	702,300 kJ
Velocity of Advance Rate	50 - 200 m/hr.
Discharge Stack Temperature	750 C

Test Methodology

The test site consisted of a test beach six meters long and fifty centimeters wide. Grain size used ranged from fine sand to 2.5 centimeter gravel. The test burner was positioned over the beach on two "wheel-rail" arrangements. The rate of advance was controlled by a tow line and winch.

The tests run attempted to establish the efficiency of the removal of oil from the beach relative to the amount of energy applied in the form of heat. The test beach was sufficiently flooded in order to maintain a high water table and minimize the penetration of oil.

Waste oil used in the tests were Alberta Crude and #6 Fuel oil. Emulsifications of each oil were also tested.

Tests were also conducted by enriching the oxygen content of the auxiliary blower air. Oxygen enrichment was found to increase the overall internal temperatures and improve combustion. It was concluded however, that the extra operating costs outweighed the small benefit of its use.

Results and Conclusions

From the results, it is apparent that the Bennett Beach Burner can significantly reduce the amount of oil left on a beach. The percentage of oil removed is dependent upon the beach type, with an increase in removal rate occurring with a reduction in particle size. Sand was cleaned more completely than gravel, which in turn was more completely cleaned than cobble. A beach with a high water table is more effectively cleaned than one which is well drained.

The efficiency of the burner is virtually unaffected by the type or condition of the oil it is exposed to. However, with high viscosity oils such as bunker, there is a requirement for a reduction in speed to allow for a greater period of time for vaporization to take place.

The equipment operator can visually ascertain the most suitable rate of advance.

With an average rate of removal of 76% on thinly coated beach material, the amount of oil remaining is minimal. This remaining oil is below the beach surface. Under some operating conditions the beach will be left with a black spot (presumably coke) coating the beach surface. This is loosely adhered to the beach material and would presumably be dispersed in a few tidal cycles.

The depth of heat penetration into the beach is minimal in a normal operating pass and is hand touchable within a few minutes. See photos 1, 2 and 3 of a typical test.

We have extrapolated the average results obtained from the prototype beach burner to determine the cost of cleaning one hectare of beach. These results indicate a cost of approximately \$8,700/hectare. The costs of providing manual cleaning or mechanical equipment are significantly higher.

Both of these latter methods must also include a cost for the disposal of the oil residue.

An examination of the effects of the beach burner on beach organisms has not been undertaken. It is obvious that surface organisms will be obliterated, however, due to the low level of heat penetration into the beach and the greatly reduced level of oil contaminates, the subsurface survival rates should be greatly enhanced. With appropriate low pressure contact vehicles, the change to the beach structure will be significantly less than for other clean-up techniques.

As a result of these tests, the basic data exists for the design of a full size model. The structural temperatures encountered do not preclude the use of aluminum for construction of a lighter unit.

Overall the use of an "in-situ" combustion unit, utilizing the concepts examined in this trail, appears to be an operable, cost effective means of removing stranded oil from shorelines. The system can be lightly constructed, helicopter transportable, and requires the very minimum of support personnel. Meeting these criteria, such a unit will be appropriate for use in remote locations.

Test results and data from this study can be obtained by contacting Bennett Environmental Consultants Ltd., Vancouver, British Columbia.

PHOTOS



PHOTO 1 - SEPTEMBER 19 - TEST # 6
SAND/GRAVEL BEACH AFTER OIL SPILL.

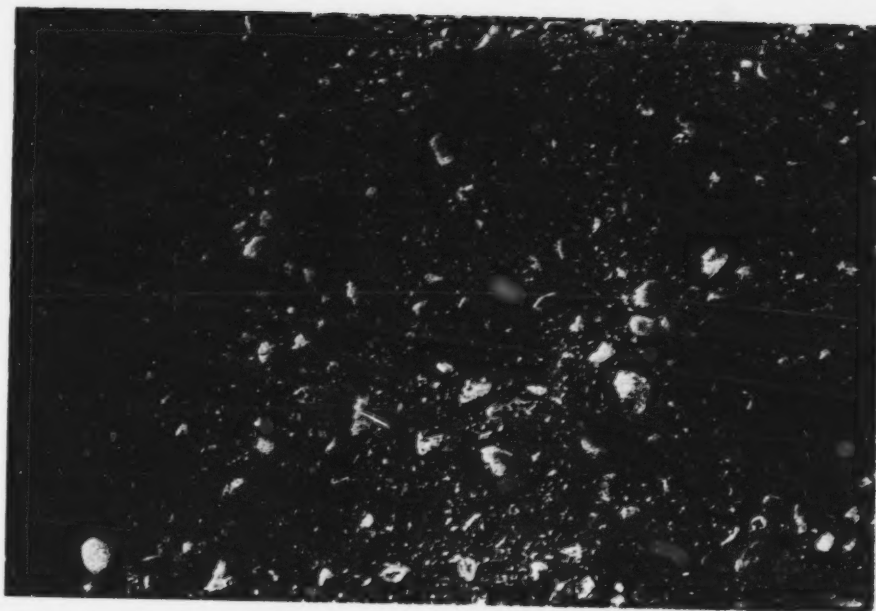


PHOTO 2 - SEPTEMBER 19 - TEST # 6
SAND/GRAVEL BEACH AFTER BURN.

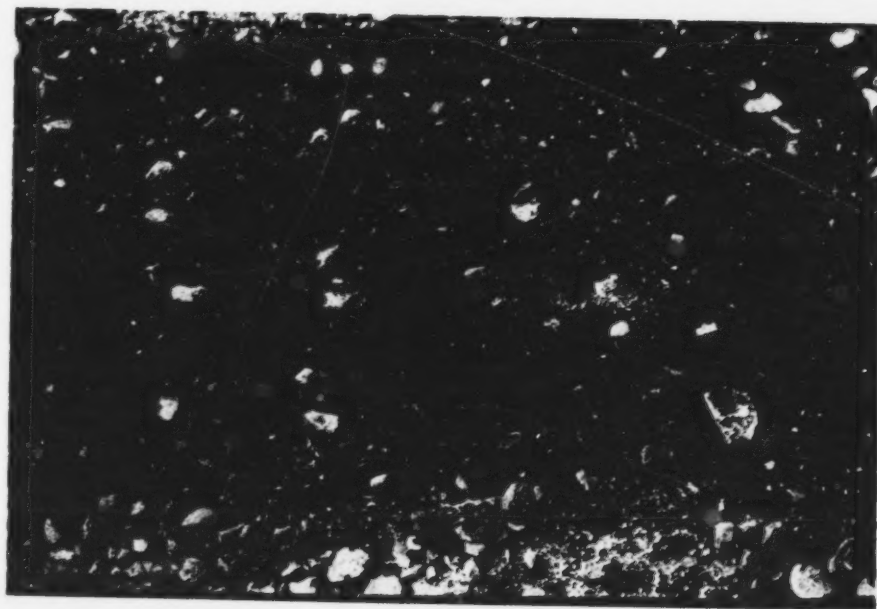


PHOTO 3 - SEPTEMBER 19 - TEST #6
SAND/GRAVEL BEACH AFTER BURN WITH TOP 70 mm OF SUBSTRATE.

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IN SITU BURNING OF OIL IN ICE LEADS

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ABSTRACT

A series of experiments was carried out at the Esso Research ice basin in Calgary, Canada to evaluate the critical parameters of burning oil in ice leads. This may be a useful spill cleanup technique in the Arctic under certain conditions. Twenty-five test burns of Norman Wells crude were carried out to study the effect of wind herding, oil weathering, oil thickness, and lead geometry on burning efficiencies. Burning efficiencies of up to 90% were measured where moderate winds herded the oil into long narrow leads. Burning in other lead geometries was less efficient as was burning in the presence of brash ice. Weathering of the oil up to 20% did not significantly effect the burns.

INTRODUCTION

Oil spill cleanup in Arctic waters poses unique problems because of the total or partial coverage of ice for much of the year. If oil is lost beneath the ice surface, such as might occur with an underwater pipeline break or well blow out, the oil would collect in rough areas of the ice sheet lower surface. In regions where the Spring breakup occurs, it could then percolate through the ice to form in melt pools. Otherwise, it would reach the surface only when leads open up around pressure ridges, either in the multi-year ice or in transition zone ice. Because such leads may be short lived and occur in remote areas, oil clean-up would be very difficult under the best circumstances.

In remote areas such as the Arctic, the transport and disposal of collected oil and debris becomes a problem of similar scope to that of containment and pick up. Hence, the burning of spilled oil in-situ appears to be a simple and straight forward solution. Several recent studies have addressed various aspects of in-situ burning, particularly with respect to oil in melt pools. Dickens and Buist (1981) reported on a field study of oil clean-up in ice infested waters conducted under the auspices of COOSRA, in which the burning of oil in melt pools was studied. The OHMSETT facility in New Jersey has been used to determine burning rates and burning efficiencies of oil in broken ice with varying ice coverages. Energetex (1981) studied spreading rates of oil on water and the effects of wind herding. Buist and Twardus (1984) conducted theoretical and laboratory studies on oil and flame spreading under differing wind conditions. To date, the one area of burning as a clean-up technique in ice infested waters that has not been addressed is that of the efficiency of burning of oil in ice leads.

In order to evaluate the parameters of burning which are likely to be critical in ice leads, a series of experiments was carried out in February 1986 at the Esso Resources ice test basin in Calgary. The tests were designed

to evaluate the effect of wind herding, oil weathering, oil thickness, lead geometry, and presence of brash ice on burning efficiency. The size of the facility allowed burning experiments to be carried out at essentially full scale.

TEST FACILITIES AND EQUIPMENT

The Esso ice test basin is a large outdoor concrete pool 30 meters wide by 56 meters long and varying in depth from 0.75 to 3 meters. Water capacity is approximately 2200 cubic meters. Two 200,000 BTU/hour refrigeration units are available for forming the ice sheet, although for the oil in ice leads burning experiment, the sheet was allowed to form naturally.

A device was designed and constructed to measure the thickness of oil on water. It consisted of a hollow aluminum bar 5cm. by 12cms. in cross section and 1.5 meters long, with leveling feet at each end. A sliding trolley, which runs along the beam but is electrically isolated from it by teflon bearings, holds a digital readout micrometer screw. One lead of a sensitive ohmmeter is attached to the micrometer screw while the other lead is grounded to a large paddle which extends from the aluminum bar into the water below the oil slick. The device detects the oil-water interface by measuring the change in resistivity as the micrometer screw is turned vertically through the oil to the water. In laboratory tests the reproducibility of oil thickness measurements with the device was $\pm 0.03\text{mm.}$ Under the best lighting conditions, the device always detected the oil-water interface before the screw tip was visible below the oil.

In order to determine heat fluxes into the water and ice from the burning process, an underwater rack was constructed which held 6 thermocouples and 6 thermistors. Each thermal device could be raised or lowered to a preset depth or imbedded in the ice at the side of the lead. All outputs were connected through a sheathed cable buried in the ice to a Sea Data Inc. Model 1250 logger. The signals were digitized at a one second rate and recorded on magnetic tape for later analysis.

Wind was provided by a 17ft. airboat. It used a 150hp. aluminum V6 engine to drive a 54 inch blade at 1000 to 3800 rpm.. The entire unit was light enough to be easily moved across the ice surface to any desired location. Generally, winds could be controlled to within ± 0.5 m/sec. of the desired velocity provided that local winds were calm. This was insured by erecting fences consisting of 4 by 8ft. plywood sheets parallel to the ice leads 1.5m from each edge. To obtain very low winds it was necessary to erect a lattice baffle immediately behind the airboat so as to reduce the air flow. A hand held anemometer was used to measure the air flow 20cms above the water surface.

Each burn was recorded on colour video with a portable Hitachi camera mounted on a tripod. Some experiments were monitored with a Barr and Stroud Model IR18 infrared camera operating between 8 and 13 microns wavelength.

PROCEDURES

During November and December 1985, the ice sheet on the outdoor basin froze naturally to an average thickness of 45cms. Chain saws were used to cut several artificial leads in the sheet. For most experiments these were 1 by 10 meter leads, but a semicircular hole 5m in diameter, a square hole 5m by 5m, and two triangles each with a 1m base and 4m perpendicular were also cut. Typically the water surface was 3 to 4cms. below the top ice surface.

Once the lead was clear of brash ice, the temperature sensing array was lowered into the lead and the sensing elements adjusted for correct heights. Aged Norman Wells crude (from 10 to 40 litres) was then poured carefully on the lead surface and allowed to spread under the experimental wind conditions selected. After approximately 15 minutes, equilibrium thicknesses were obtained and thickness measurements were then made using the device described previously. The wind was measured about 20cms. above the oil surface and adjusted by varying the airboat engine speed. Wind speed was always set at the front edge of the oil slick.

The Norman Wells crude was aged by purging the oil in barrels with a stream of compressed air. The degree of weathering was estimated both from the loss of oil from the barrels and from simulated distillation gas chromatography.

Oil was ignited with a small hand held torch, usually at the upwind edge of the slick but occasionally at the down wind edge. The progression of the flame front was then measured with a stopwatch as it passed meter marks at the edge of the lead. When burns took place in irregular leads, a sketch of the burning front at regular intervals was made and later checked for accuracy by viewing the video tapes.

After completion of a burn, the residue was removed from the lead, placed in plastic bags, and weighed. This could usually be done using sieve shovels which would lift the viscous residue and allow the water to drain off. Residue recovery was estimated to be better than 95%.

Samples of lead water were taken for hydrocarbon analysis both before and after the burn. Residue samples were saved for later analysis.

A total of 25 burns were carried out during January and February 1986 in which the parameters studied were wind herding, oil weathering, slick thickness, and lead geometry. Two experiments were conducted in the presence of brash ice.

RESULTS AND DISCUSSION

General

The processes which occur during the burning of a combustible liquid are very complex but depend on the rate at which heat is transferred to the fuel, the rate at which fuel is carried to the flame, and the rate at which oxygen can be supplied to the flame and combustion products removed. These various processes could be observed during the experimental burns carried out in the

ice leads. A typical burn sequence began with the ignition of one end of the oil slick. Initially the fire spread slowly often with small visible blue flames at the base of slightly larger (10 to 15cm.) yellow flames. At this point whatever light ends were available (depending on the oil type) were burning. As sufficient heat was transferred to the slick to vaporize heavier components the flames increased in size and began to spread more rapidly. Within about one minute after ignition, the fire had usually reached one square meter in area with flames a meter high. At this point rapid boiling of the lead water would commence accompanied by popping noises and a marked increase both in flame size and spreading rate. It appeared that the violent agitation of the water caused by the boiling served to increase the rate at which fuel was supplied to the fire. Voluminous black smoke accompanied this phase. There was no evidence that the initial fuel type had any effect on the fire by the time it had matured to this stage. Depending on wind speed, air would often be entrained to the extent that a firestorm would develop and the flame would take on the characteristics of a miniature tornado. This stage of the fire continued as long as there was fuel available. Finally, as fuel was exhausted, the fire would very rapidly die down to a few scattered small blue flames which might persist for a minute or more before extinguishing. Rapid cooling of the residue followed.

Wind, oil weathering, amount of oil, and lead geometry have been varied and the effect of these on oil burning in ice leads measured by calculating the flame spreading rate, the burning regression rate, and the burning efficiency. In addition, the viscosity and specific gravity of the residues have been measured and gas chromatographic analyses made. The lead waters have been measured for hydrocarbon content. Many of these analyses and measurements are summarized in Table I and will be discussed in detail below.

Wind Herding:

Wind may be very advantageous for burning oil in leads by herding thin sheens of oil to thicknesses which will support combustion. In an early study of burning in melt pools, Energetex Engineering (1977) showed that low winds would herd oil, which was otherwise too thin to burn, to sufficient thicknesses for burning. They determined that without wind, fresh slicks had to be thicker than 0.6mm to burn and heavily weathered oil had to be at least 3mm thick to burn. We studied slicks from 1.0 to 4.0mm thick. In the Beaufort, winds average 3 to 5 meters/sec. Studies by Dome (1981) show that the ground wind shear over level ice causes the 10 meter height wind speeds to be approximately halved at ground level. Thus to mimic realistic Beaufort winds, experiments should be carried out with ground winds of about 2.5 meters/second.

The average wind herded oil thicknesses calculated on the basis of the amount of oil spilled and the observed oil coverage are shown in the table. These calculated values agree well with the average of the thicknesses measured with the device described previously. The herded thicknesses are in general agreement with those reported by Energetex(1977). Buist and Twardus (1984) find that 1 hour weathered oil 2mm in depth will be herded to about 3mm with a 1 meter/sec. wind, which agrees well with the measured value in experiment #13.

TABLE I RESULTS OF BURNING EXPERIMENTS

Oil Weathering %	Test #/Conditions	Volume Spilled ℓ	Wind Speed m/sec	Burn Time After (sec) Ignition	Residue Volume ℓ	Burn Efficiency %	Herded Slick Area m^2	Regression Burning Rate mm/min.	Flame Velocity m/sec.
5 ↓ 10 ↓ 15 ↓ 20	10	30	--	271	3.2	89	9.6	0.6	0.05
	13	20	1	189	4.7	77	7.3	0.6	0.12
	15	30	2.5	290	4.1	86	7.8	0.7	0.15
	4	30	1.5	158	3.8	87	5.7	1.7	0.05
	5	30	--	358	4.5	85	8.1	0.5	0.04
	6	20	--	199	5.8	71	9.0	0.4	0.07
	7	40	--	375	6.5	84	10.0	0.5	0.03
	8	10	--	356	3.3	67	3.7	0.3	0.03
	9	30	2.5	226	3.1	90	3.2	2.2	0.07
	16	30	--	303	4.4	85	9.5	0.5	0.05
15 ↓ 20	20	30	0.5	346	2.5	92	4.0	1.2	0.03
	17	30	2.5	195	3.0	90	3.0	2.7	0.08
	23	30	--	277	5.7	81	7.4	0.7	0.04
	21	30	1.4	201	4.9	84	4.5	1.6	0.03
	25	30	5.8	225	4.7	84	1.6	4.1	0.07
~10 ~10 5 ↓ 15	2 } Brash	27	--	885	8.2	70	9.0	0.1	0.01
	3 } Ice	27	4.5	565	5.4	80	5.0	0.4	0.03
	24 Circle	30	3	189	5.4	73	3.5	2.1	--
	22 Crosswind	20	4	305	6.6	78	9.8	0.2	--
	11 Square-Centre	30	--	161	9.1	70	12.6	0.5	--
	12 Square-Side	30	3	414	7.5	75	5.5	0.6	--
	14 Square-Corner	30	3.5	467	7.9	74	5.5	0.5	--
	18 Triangle-Downwind	20	2	174	2.3	89	2.7	2.2	0.11
	19 Traingle-Upwind	20	2	574	2.6	87	2.7	0.7	0.01

Flame Spreading Rate:

One would anticipate that the rate at which the flame front spreads along an oil slick would depend primarily on the wind speed and degree of oil weathering. The rates shown in Table I are averages measured between the time the flames covered the first square meter of the slick and the time the flame front reached the end of the lead. No values are calculated for the square or circular leads. All results for oil thicknesses of 3mm in rectangular leads are plotted in Figure 1(a). As expected there is a general increase in flame spreading rate with increasing wind speed and a dependence on degree of oil weathering. However, the latter is not marked once the weathering exceeds 10%. Presumably the flame spreading rate depends on the amount of light ends in the oil available to preheat and vaporize the remaining material, and most of these have been lost after 10% weathering. The presence of brash ice significantly slows the flame front as can be seen by comparing the values in Table I Trial #3 (with ice) to Trial #9. Finally, from Figure 1(b) it is clear that the amount of oil spilled, once it is thicker than 3mm (in this work, 30 l spilled), does not affect the flame speed. The graph suggests that a 2mm thickness is optimum but more tests are needed to confirm this finding.

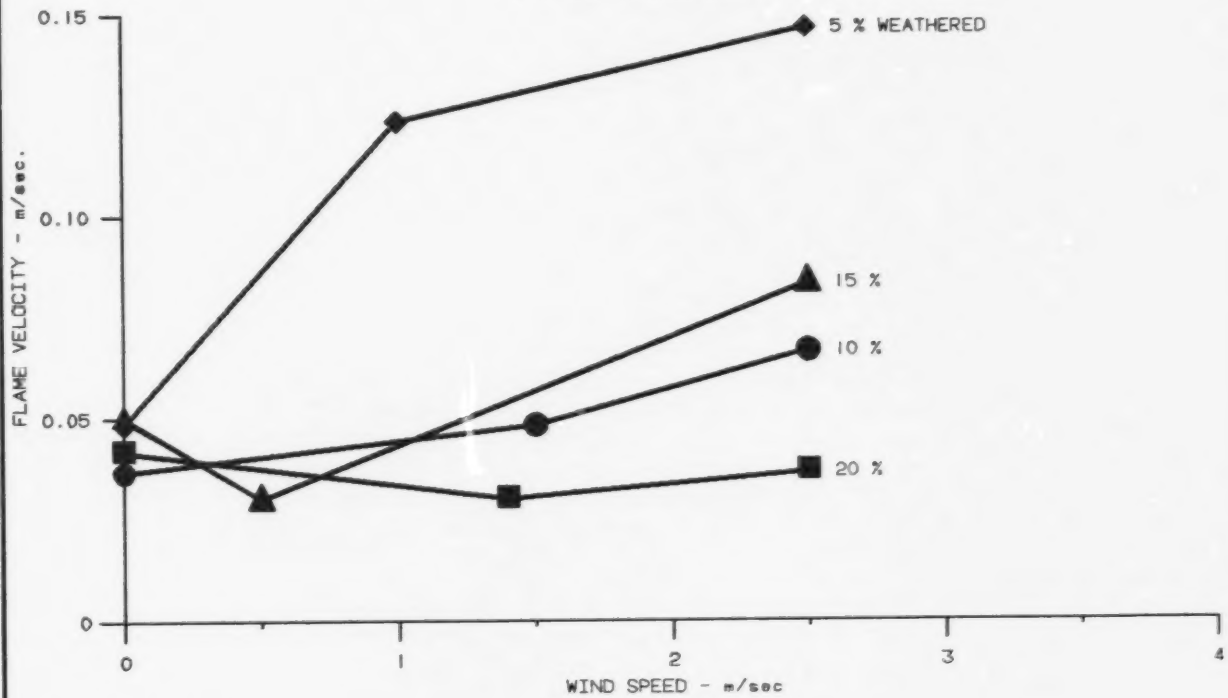
These results are in general agreement with the work of Buist and Twardus (1984). Their results from wind tunnel experiments using Alberta Sweet Mixed Blend crude show a linear relationship of flame velocity with wind speed and a dependence on oil aging. For approximately 10% (8 hour) aged crude they measured the flame speed to be 3m/min. at a wind speed of 1.5m/sec. and about 4m/min. for a wind speed of 2.5m/sec. Considering that our experiments were conducted outdoors at real scale where it is very difficult to control the wind, the results are remarkably similar. The two oils have similar viscosities and normal alkane distribution. In both sets of experiments the thickness of the spilled oil was 3mm.

Temperature measurements of the water, ice and air as the flame spread down the lead were also taken, usually at the 8 meter mark of the lead. An example of these temperature profiles is shown in Figure 2(a) Probe numbers 4 and 6 were located in the oil and number 5 was one centimeter higher in the flame. Other probes were placed from 3 to 8cm. below the water level and show a temperature rise of up to 5 degrees C. as the flame front passes over. Usually this maximum occurs about one minute after the front arrives. From a number of similar profiles some preliminary measurements have been made. These indicate that the flame duration is shorter when a wind is present and the water returns to its original temperature more quickly. It appears that the maximum flame temperature may be higher however. When the oil thickness was 2mm. rather than 3mm. the flame duration was shorter and, as might be expected, the water temperature rose less. In a light wind the temperature rise of the water from burning 15% weathered oil was greater than from burning 20% weathered oil. Further analyses of these profiles and video image analysis of the flames is continuing.

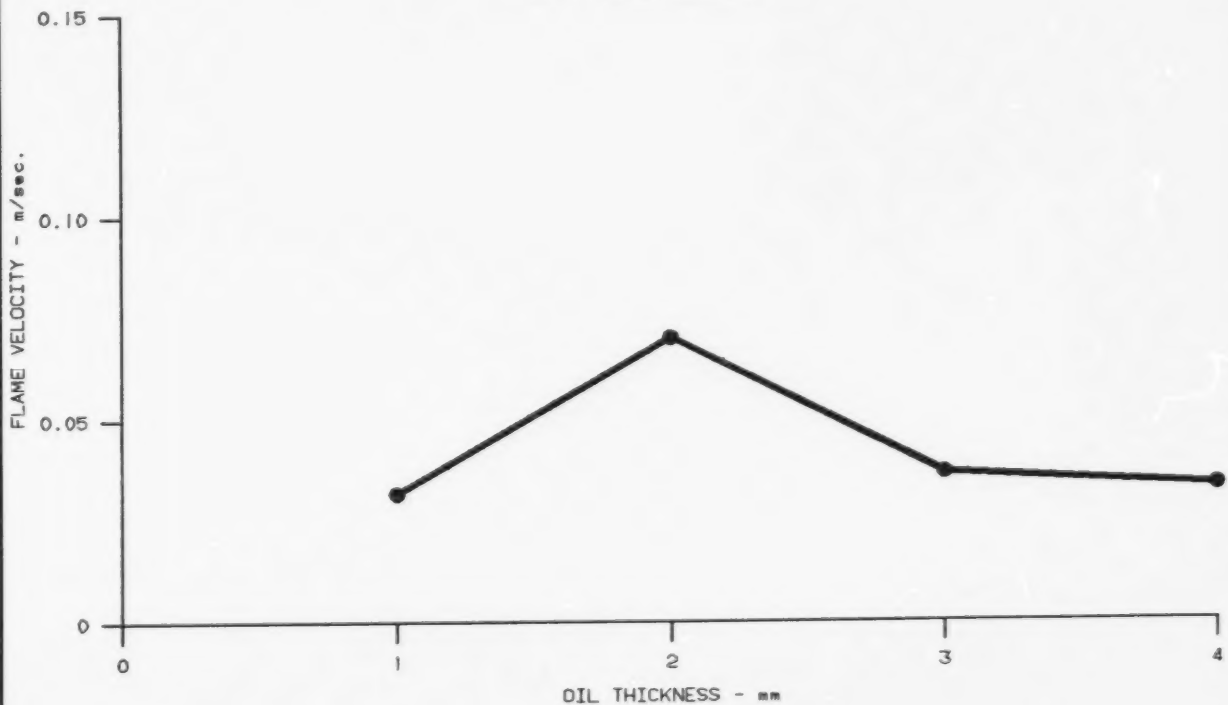
Figure 1

ESSO RESOURCES CANADA LIMITED
FLAME VELOCITY

3.0 mm THICKNESS



10 % WEATHERED



Regression Burning Rates:

Average regression burning rates have been calculated as a measure of the speed with which a given oil slick can be burned under different wind conditions. These were calculated from the wind herded areas of the oil before ignition and the total burning times after the fire had become established. Rates are listed in Table I, and for 3mm oil thicknesses in the rectangular leads, are graphed in Figure 2(b). It can be seen that for a given oil type there is a linear relationship between the wind velocity and the regression burning rate. This may be due to the herding which thickens the oil and promotes more efficient transfer of heat from the flame to volatilize the remaining fuel. In addition the wind insures that the fire is not oxygen limited. Curiously, the graph shows that the more weathered oil burns at a faster rate. This phenomenon may be related to the mechanics of heat transfer to the remaining fuel as well. It is clear from experiments #2 and #3 (Table I) that the effect of brash ice, which would be expected to impede the heat transfer, dramatically decreases the burning rate.

The effect of lead geometry is not quite as apparent. Where wind herding can confine the oil such as in the apex of a triangle (test #18) or along the circumference of a small circle (test #24), the burning rates are similar to those in the long rectangular leads. Unconfined slicks such as along the side of a large square lead (test #12) or in the centre of an open area (test #11) have lower burning rates.

There are no exactly comparable measurements in the literature but Buist and Twardus (1984) have measured the regression rates of fresh Alberta Sweet Mixed Blend crude under calm confined conditions and find that the rates vary from about 1.0 to 2.0mm/min. These are for oil thicknesses of 4 to 40mm, that is, much thicker than reported here. Nevertheless, the rates are similar to our thinner weathered oils. We observe a similar trend of regression rates with oil thickness for calm conditions as they report but with lower absolute values. Likewise, in small scale laboratory tests, Smith and Diaz (1984) report burn rates of 0.2 to 0.4mm/min. for 2.5 to 10.5mm deep fresh Prudhoe Bay crude.

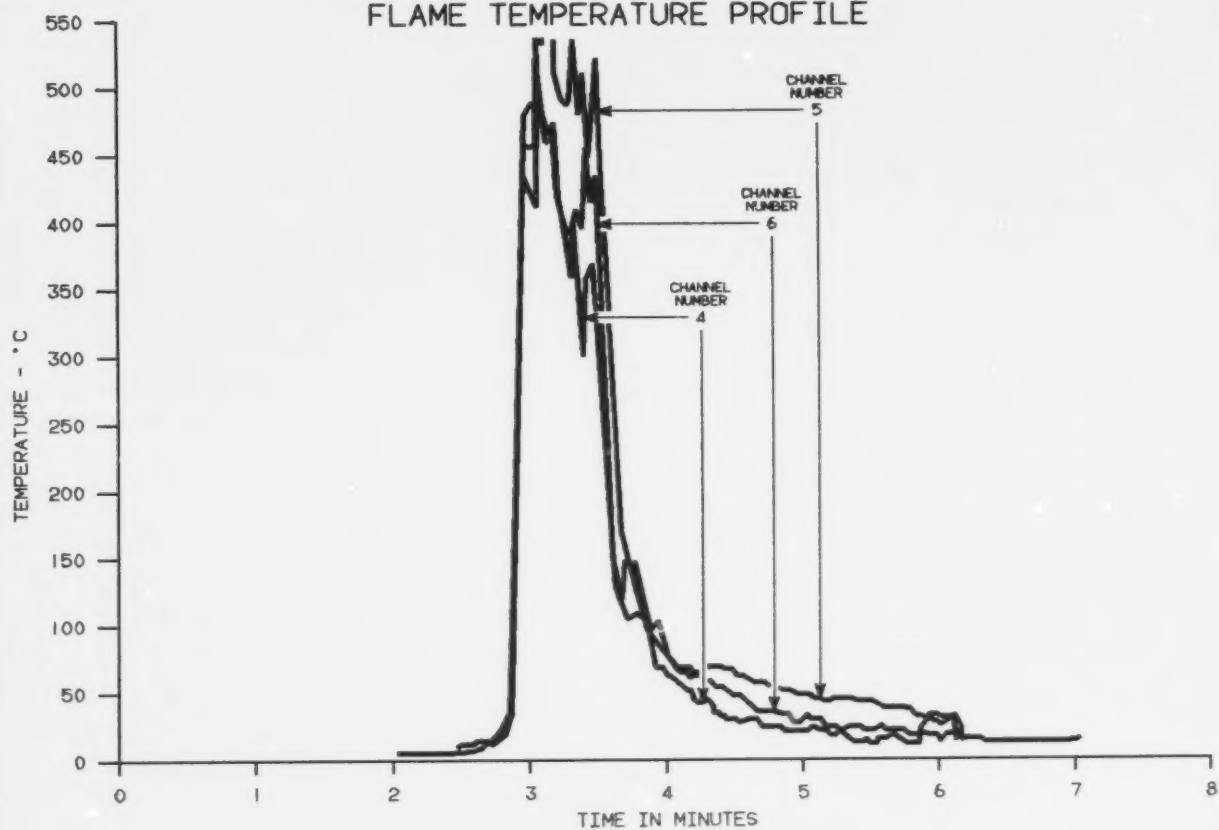
Burning Efficiencies:

In Figure 3(a) the calculated burn efficiencies as a function of wind speed and oil type are summarized for 3mm depth oil in rectangular leads. These are based on the weight of the burn residues and their specific gravities. While all of the efficiencies are high, there is a slight overall increase with wind speed. There does not appear to be a consistent dependence on oil weathering, except under calm conditions where there is a slow decrease with increased weathering (Figure 3(b)). Figure 3(c) shows that the efficiency increases with the amount of oil burned, at least to a depth of 4mm.

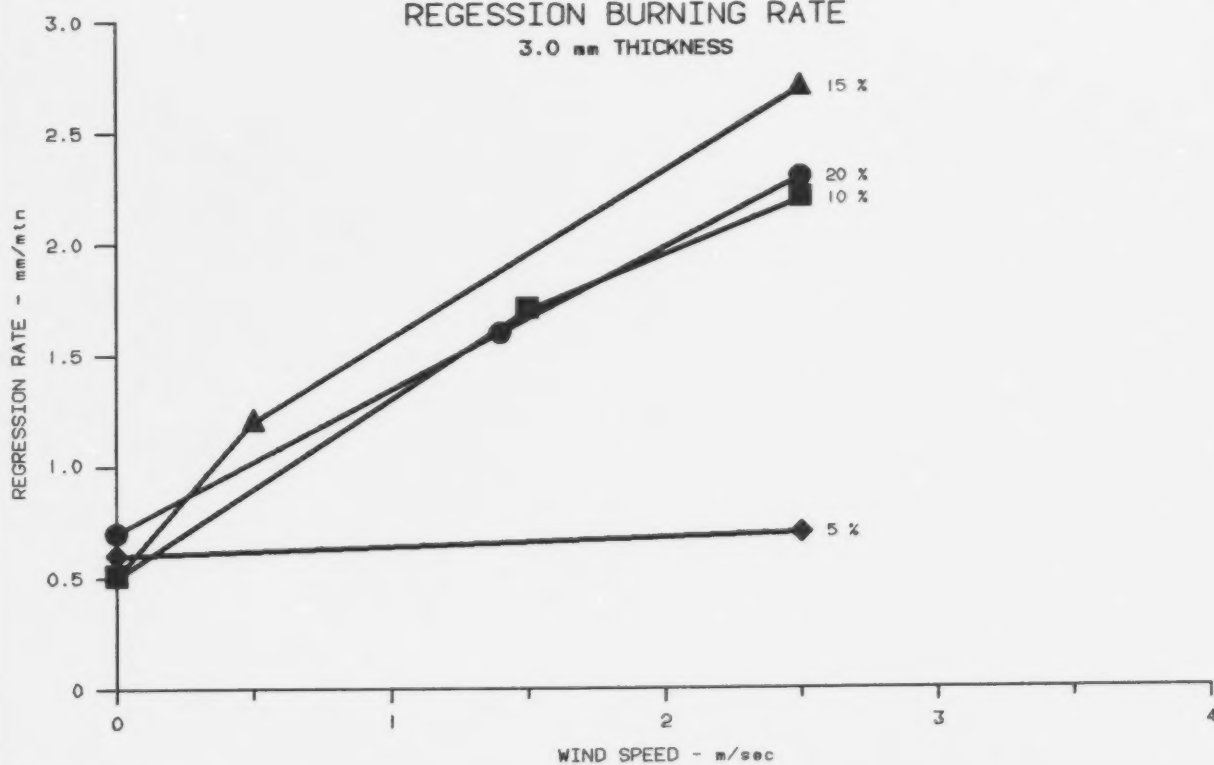
The efficiencies for other tests listed in the table show that the lead geometry is important for good burning. Where the oil can be confined by herding (such as at the apex of a triangle - test #18 and #19) the efficiencies are comparable to those in straight leads. For more open leads where the oil is herded along a straight edge, the efficiencies are 10 to 20% lower (tests 11, 12, 14, and 24). In test #22 the wind was directed across a 1

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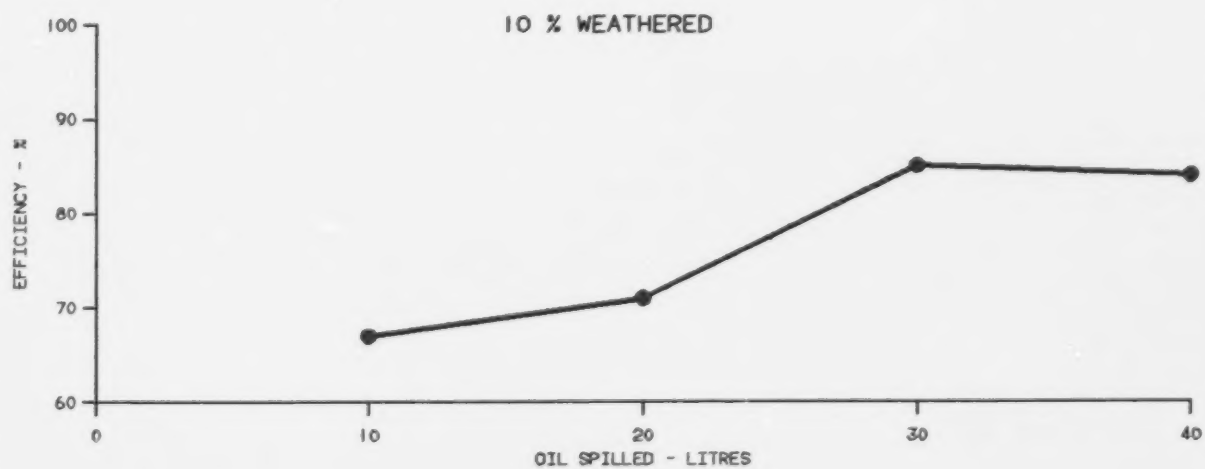
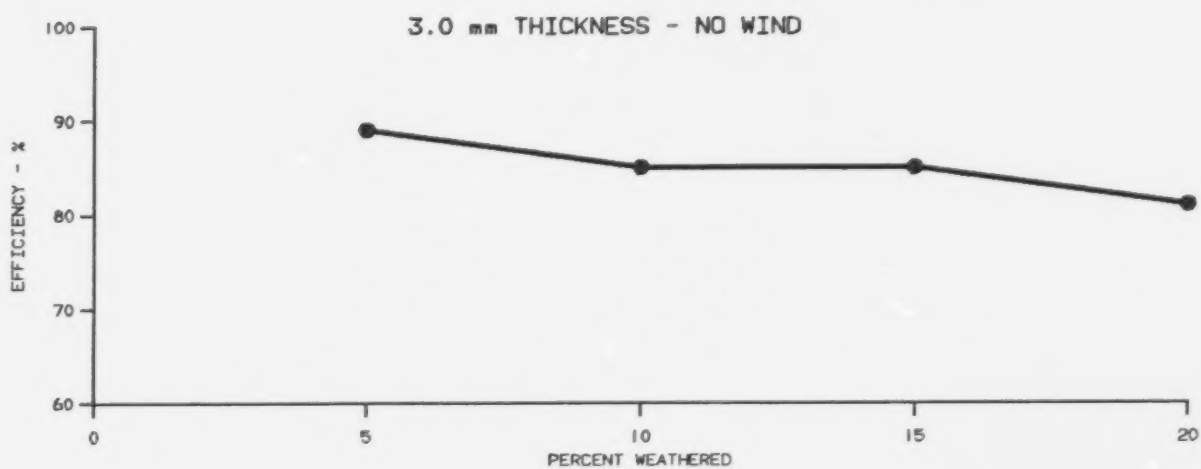
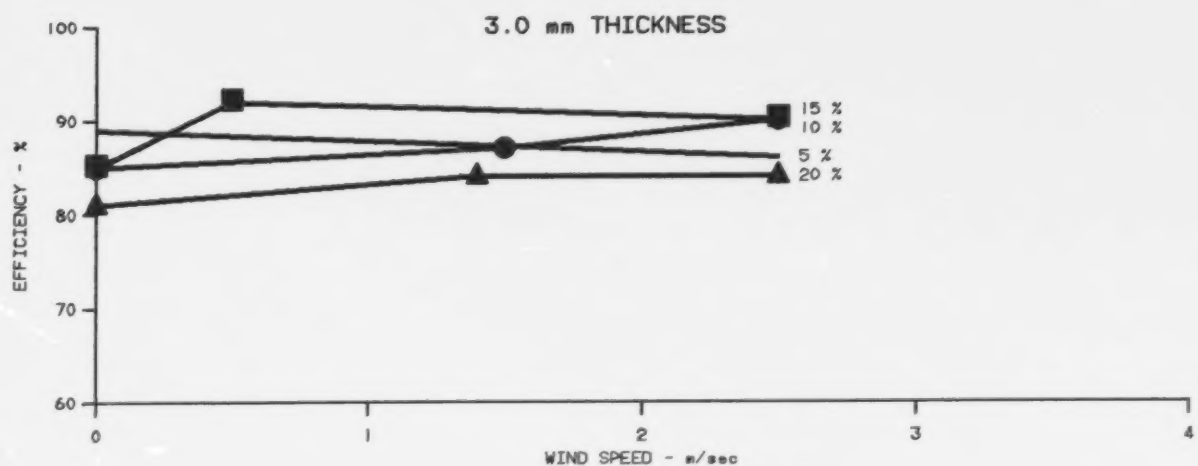
FLAME TEMPERATURE PROFILE



REGRESSION BURNING RATE 3.0 mm THICKNESS



ESSO RESOURCES CANADA LIMITED
BURN EFFICIENCY



x 10m lead where the ice height above the water was 3cm. In this case, despite a 4m/sec. wind, no herding was observed and consequently, the efficiency was similar to test #13 where the wind was very low. Apparently the 3cm ice height above the water was sufficient to shield the oil from the wind.

Brash ice also decreases the burning efficiency by retarding herding. Smith and Diaz (1985) report 79% efficiency for weathered Prudhoe Bay crude in 4m/sec. winds and 75 to 84% ice cover. These conditions would be similar to our test #3. Buist and Twardus (1985) report an 88% efficiency for a large scale confined burn of fresh Prudhoe Bay oil with a 0 to 2m/sec. wind, again a value similar to a number of the runs reported here. The field trials conducted in the Beaufort by Dome (1981) in which oil percolated from below the ice into melt pools resulted in burning efficiencies of 18% to 77 %. In some instances wind herding was an important factor and oil thicknesses up to 5cm. were reported.

SUMMARY

Oil spill cleanup in Arctic waters poses unique problems because of the presence of ice and the remoteness of potential spill sites. This work investigates the removal by burning of spilled oil in leads. Twenty-five burns of weathered Norman Wells crude were carried out under varying wind conditions in leads cut in an ice sheet. It was found that burning efficiencies of up to 90% were possible if moderate winds (similar to average Beaufort winds) herded the oil into long narrow leads. For leads of other geometries with similar winds, efficiencies might be as low as 70%. Winds of up to 4m/sec. across a narrow lead caused no oil herding and resulted in low efficiency burns. Brash ice impeded wind herding of the oil and resulted in lower burning efficiencies. Wind herded oil could be ignited at either the upwind or downwind edge with similar burning results. Weathering of oil of up to 20% did not significantly affect the burn efficiency in moderate winds.

Further analysis of water, ice, and flame temperature data, as well as residue composition and viscosities is continuing.

ACKNOWLEDGMENTS

This work was carried out under a grant from the Environmental Studies Revolving Funds. We wish to acknowledge the help of R.A. Paterson who was responsible for the operation of the ice test basin.

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TRIALS WITH NET BOOM FOR CORRALLING AND RECOVERING VISCOUS OILS AT SEA

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SUMMARY

This paper describes experimental work conducted in the southern North Sea to collect viscous emulsion using a 1 km length of the 2 m wide Jackson netting as a semi-permeable boom. In one exercise 21.5 tonne of viscous emulsion was put on the sea and some 20 tonne of this emulsion pumped back on board the recovery vessel RV Seaspring after having been surrounded by the net and left to float with the current for nearly 24 hours.

The work was co-funded by the European Community and the Marine Pollution Control Unit (MPCU) of the UK Department of Transport.

BACKGROUND

The discovery of the Beatrice crude oilfield in the Moray Firth provided an impetus to search for better ways to recover viscous and semi-solid oils. This field gives a crude oil that is very waxy and which solidifies on the sea when the sea temperature is below about 15°C. A simple trawling system for oil recovery, based on an earlier Japanese design, was developed by the British National Oil Company (now Britoil PLC) and Warren Spring Laboratory (WSL). A Mr J. West of Gardenstown, Scotland, who was involved with the use of these trawl nets suggested in 1981 that instead of using comparatively small net bags each capable of holding about 1 tonne of oil, the purse seine netting principle could be adapted to enable much larger quantities of oil to be collected. For the oil recovery application however the net could be quite shallow but would need to have freeboard in contrast to the fishing application.

During early trials^{1,2} in 1982 with Mr West's idea a loop was made with about 50 m of net from the side of the RV Seaspring and 4 barrels of an emulsion released into the area of sea surrounded by net. The net was slowly recovered and as the oil was brought to the side of the ship the oil was taken off using the Springsweep Airlift recovery system.

The success of these trials, especially the recovery of oil, showed that the concept of corraling viscous oil on the open sea ought to be feasible.

Corraling of Oil

The scheme for recovery of oil originally suggested by Mr J. West was to release net around the oil in the manner used by a Seine Purse fishing boat, and to haul in the net to recover the oil. This scheme was adapted subsequently to allow the deployment of several fishing boats, each carrying perhaps ½ km of net, so that a very long length of net could be joined together in the sea in order to surround the spill. The net would gradually be recovered by a larger vessel (mother ship) and the oil taken up by a suitable recovery system.

In the event of bad weather the net surrounding the oil would be closed by joining the two ends and the whole system allowed to float with the oil until the weather improved sufficiently for recovery operations to be undertaken.

Following the WSL trials³ an alternative method of collection can be considered. Instead of surrounding the oil with net, the so called corraling operation, the net can be towed very slowly (ca 0.2 knot) in a U formation into the prevailing wind to enable the oil to drift into the U of the net formation. After collecting the oil in the net, the tow lines can be passed to the recovery vessel, for net and oil recovery to take place. The net boom clearly behaves differently to an impervious boom as most of the water passes through the net (except at the water level) and the downward current which carries oil under a conventional boom does not occur to the same extent with the net boom.

EQUIPMENT USED

Net Boom

Generally, the net consists of a double layer of 2 m wide netting (1 mm apertures, Fig. 1) with towing warps sewn into the netting at top and bottom (Table 1). The towing warps are held apart by 25 mm dia nylon poles, at 1 m intervals, which are secured to the warps by stainless steel clips ("J" bolts). Each nylon pole has a permanently air-filled buoyancy sphere midway along the pole, and ballast of circular lead weights on the bottom of each pole.

The quality of the new netting supplied was considerably better than that of the existing MPCU netting acquired for the 1982 tests which had a tendency to tear if snagged.

Two 500 m lengths of boom were used for the trials, the first length (called the old net) consisted of 100 m of new improved netting joined to the existing MPCU netting, and the second length (called the new net) was entirely new (see Table 1).

TABLE 1. - Containment Boom Characteristics

Overall height	2.0 m
Free board	1.0 m
Draught	1.0 m
Weight/m	9.6 kg
Tensile strength, total	6.26 tonnes
Net fabric	Double layer type 66 nylon, 840 denier knotless net reinforced top and bottom with polyester banding incorporating 14 mm warp
Buoyancy	9.5 kg per unit
Poles	Type 6A nylon tubes at 1 m intervals
Ballast	14 lead rings of total weight 3.13 kg/pole

Hydraulic Roller

A hydraulic roller system, designed by Fishing Hydraulics (Scotland) Ltd in co-operation with Jackson PD Ltd, is used to transfer the net out of an ISO container or a ship's hold into the sea and for the recovery operation.

This unit, which weighs approximately 500 kg, has a main roller 2.1 m long and 0.34 m dia. At each end of this roller smaller stub rollers, 0.5 m long and 0.27 m dia, run in contact with the main roller so as to grip the net between pairs of rollers. Both the main roller and each small

roller are driven independently from a hydraulic power supply providing 50 l min⁻¹ of fluid at a pressure of up to 120 bar. The supply of fluid is controlled by a valve arrangement and can be reversed as required.

The two stub rollers are loaded by hydraulic pressure onto the main roller and can be lifted off to clear any snagging of the net.

For the experimental programme the two standard open top (6.3 m long) ISO containers were modified by fitting lugs so that the hydraulic rollers can be placed above the doors to facilitate top loading.

RV Seaspring and MFV Alison Jane

The trials were conducted from the Department of Trade and Industry's research vessel Seaspring, which is a 57 m long vessel with oil storage facilities. The vessel with a beam of 11 m and a 1057 bhp main engine is fitted with a 390 bhp White Gill bow thruster which can be controlled at the bow of the vessel. The recovery requires that the incoming net comes aboard at right angles to the ship, and the bow thruster is essential for any successful recovery.

The 14.4 m long wooden carvel built fishing vessel Alison Jane, was chartered for a two week period to provide an auxiliary vessel capable of towing the net and acting as a support vessel for the corralling exercises. The vessel is typical of an inshore fishing craft and was chosen to show that these craft can conduct a netting deployment. The vessel had a crew of three and is powered by a 150 hp Gardiner engine driving a single screw. Her maximum speed is given as 9 knots.

Remote Sensing Britten Norman Islander

The MPCU Islander fitted with Side Looking Airborne Radar (SLAR) and a combined Infra Red/Ultra Violet Line Scanner (IR/UVLS) was made available for two surveillance flights to assist with the co-ordination of the encirclement of the oil.

Although the aircraft used the sensor equipment, its main role was to give visual reports of the movement of the vessels and net in relation to the oil which was being encircled. On the second flight, a photographer was on board to record the operations on film.

Springsweep Airlift Oil Recovery System

The components of the Springsweep oil recovery system comprising the recovery hopper, combined pump and diesel engine, air compressor, recovery hose, and skimmer were placed on the deck so that the recovery hose could be fed out on the starboard side of Seaspring and the discharge from the hopper put into No. 2 starboard oil tank.

The prime mover of the system is a Perkins D3.152 (45 hp) diesel engine which drives a Roots Airblower SR170 displacing 21 m³ min⁻¹ air. The air blower draws air from the collection hopper, of capacity 2.2 m³, which in turn draws air, oil and water from the floating skimmer connected to the hopper by a 15 m length of 150 mm dia hose. The hopper is fitted with pneumatically operated valves which control the collection and discharge cycles between 1-10 minutes as required. The discharge of the collection hopper is accelerated by pressurising it to 3 bar during the discharge.

The skimmer is essentially an elliptically shaped mouth piece (450 x 100 mm), which floats on the sea. Two pipes of length 0.4 m, and diameter 25 mm, project above and below the mouth piece for feeding air and water respectively into the hose to facilitate the transfer of emulsion through

the hose of diameter 150 mm. The skimmer mouth piece is fitted to the hose via a swivel so that it always lays flat on the sea. Stabilising fins are fitted to both lips of the mouth so that it can work equally well with either lip in the sea.

EXPERIMENTAL PROGRAMME

Preliminary Work

Preliminary trials were conducted in July 1985 to find the best way of deploying and recovering the two lengths of net from RV Seaspring. There was insufficient space in RV Seaspring to carry both 6.3 m ISO containers on deck. The arrangement found most suitable was to store one length of net in the ship's hold and bring this up on deck when needed by having the hydraulic roller mounted on the side of the hatch and providing a slide over the ship's guardrail so that the net would slide down into the sea. The net when recovered from the sea was then re-stowed below to await final clean-up and stowage in its ISO container ashore. A space 4.7 m x 3.3 m was prepared under the hatch opening with a narrow walkway forward and aft of the space and about 1 m above the floor. This enabled men to stand on the walkway and flake out the net as it came down from the open hatch-way above. Water (and oil) drained into the bilges, but most of the oil could be retained by surrounding the net with sawdust. There was sufficient space in the hold to flake out one 500 m length of net neatly and a second length could possibly be laid on top less tidily. In the event it was not found necessary to put two 500 m lengths of net into the hold.

The second length of net was stored on deck in its ISO container adjacent to the hatch opening and could be recovered rather slowly back into this container by mounting the hydraulic roller above the closed door of the open-top ISO container.

Corralling of Oil (3rd-4th September)

The experiments to corral oil were conducted within the rectangular area in the southern North Sea where Seaspring has an exemption certificate to release oil for experimental purposes, namely within the area bounded by the ordinates 02° 20', 02° 40' E, 51° 55' and 52° 30' N.

A preliminary experiment was carried out involving the release of 5 tonne of oil to gain experience for working with a larger spill.

The testwork commenced on Tuesday 3rd September. The first task was to rehearse putting out and recovering the net with MFV Alison Jane. The 500 m length of new net which had not been put out in the preliminary trials was cast by hand from the ISO container. The vessel Alison Jane took the net in tow and a release of a solution containing 500 g of fluorescein dye was made by Seaspring for Alison Jane to try to curve the net around a visible patch. At the end of the day the net was restowed into the ISO container.

The next experiment conducted, was to put the "old" net out from the ship's hold and allow Alison Jane to take the net away so that the net stretched out in a straight line aft of the fishing vessel. Seaspring then released 5 tonnes of emulsion about midway along the extended net and, under the guidance of the observation aircraft, the fishing vessel turned and pulled the net back on itself to sweep up most of the emulsion. Both towing lines were joined, to encircle the oil, and passed to Seaspring for recovery of the net and oil.

The recovery was conducted by tying one end of the net onto a hawser

which earlier had been passed under the ship and secured to the guard rails either side; this arrangement allowed the net to be secured close to the side of the ship at water level. The other end of the net was passed over the guard rail slides and onto the roller for recovery. This arrangement was soon found to be unworkable as the two sides of the net, forming a large U, soon came together and snagged. Therefore the end tied to the warp under the ship was released and passed in front of the bow to be retied on the port side of the ship. When the majority of the net had been recovered the Springsweep airlift skimmer was put into the netted area by passing it under the net where this was lifted on board. The arrangement was not ideal, and little oil was recovered as most of the oil released had either adhered to the net and was being brought on board by the net or was encircled by the net well away from the skimmer. The ship's fire hose was used to wash the net coming on board and whilst this washed off some of the oil it created very unpleasant conditions for the recovery crew who were down wind of the spray. The recovery of oil had to be abandoned, subsequently, as the line holding the net on the port side of the ship broke after becoming frayed and the net opened allowing the oil to escape. Although almost no oil was recovered in the experiments in the first week the various procedures and manoeuvres attempted had provided valuable experience which was applied successfully to the work in the following week. It is worth noting that throughout the week there were gale warnings in force for the sea area (Thames), and the wind was SW 20-25 knots throughout almost all of the two-day trials period.

Corralling of Oil (10th-12th September)

The work programme for the second week's trials, during which a relatively large quantity of oil would be released, commenced on 10th September with the deployment of both lengths of net to form a 1 km length on the sea.

This was achieved by first putting out by hand the new net from the container on deck. As the wind was relatively light (SW force 2) the MFV Alison Jane was used to pull the net away from the ship in a north easterly direction.

When almost all the new net was out the lead end of the old net stowed in the hold was brought up through the hydraulic roller and joined to the tail end of the new net by joining the bolt ropes together with shackles and lacing the ends of the nets together. Ideally the net needed to overlap at the joint and the joint to be supported by a nylon pole, but this was not possible under the circumstances. The MFV then continued to tow the net away until the whole 1 km length was cast from Seaspring. A sea anchor was fitted to the south-westerly end of the net, and Alison Jane cast off the tow line at the north-east end.

It was observed that, when the towing tension was taken off, the net slowly sagged and the poles started to come together. Consequently Seaspring took the south-westerly end in tow and Alison Jane resecured the NE end. A rubber boat was then deployed to inspect the net and conduct repairs where pole-ends had become detached.

The net was left out overnight ready for the release of oil the next day. The arrangement was that Seaspring took the tension with the bow thruster at low thrust and pulled the 1 km length of net with Alison Jane secured to the down wind end acting rather like a sea anchor.

During the night it was realised that the current was likely to carry the net outside the area where Seaspring is authorized to discharge oil.

Consequently, Seaspring turned the whole arrangement round over a 3-hour period by towing the net and Alison Jane through a semi-circle, of diameter some 2 nautical miles, at an average speed of about 1 knot.

The arrangements for the corralling of oil on 11th September are shown diagrammatically in Figure 2 and for the subsequent recovery of the oil on 12th September in Figure 3. The net was released from Seaspring and Alison Jane maintained net tension by towing in a SW direction at about 0.2 knot. An estimated 21.5 m^3 of emulsion was discharged from the starboard side of Seaspring by flooding the tank and allowing emulsion to flow out of the deck man hole. At the same time a Framo TK-5 pump, previously lowered into the tank through the man hole, pumped the emulsion when it rose to the position of the pump to promote a more rapid discharge. After the release of emulsion Seaspring passed around the net, picked up the unattended NE end and proceeded to assist Alison Jane sweep the area of sea containing the oil.

It was found to be a surprisingly easy operation and the reports from the aircraft overhead confirmed that all the oil released was surrounded. There was some evidence of sheen coming away from the net used in the previous week's work and some oil escaped through the lacing where the two separate sections were joined together. Seaspring being the more powerful vessel did most of the manoeuvres. When the net tension increased Alison Jane found that she could not curve the net around the oil against the tension from Seaspring towing the net. Manoeuvres of Alison Jane were conducted consequently after Seaspring had let the towing tension fall.

At the end of the corralling manoeuvre Seaspring took the end cast off by Alison Jane and put this onto the port side (Figure 2E), and the other end was transferred from the stern to the position of the ISO container.

The rollers were then transferred from the side of the hold to the top of the ISO container and the new length of net recovered into the container (Figure 2F) leaving the oil contained in the 500 m of the so-called "old" net. The end of the net on the port side was then brought round to the starboard side of the ship and lifted on board where it was laced to the other end. The net now in a complete circle of circumference 500 m and containing about 21 tonnes of viscous oil emulsion was then cast free. Alison Jane then motored slowly around the net and renovated several support poles where the central buoyancy had slipped, or where ballast weights had been lost from the bottom of poles.

Once the net had no towing tension the circle very gradually contracted in size until each buoyancy chamber came in contact with the next. Considerable snagging occurred and as the contraction had not taken place symmetrically, that portion of the net without oil proceeded to collapse together completely and a long length where the two walls were in contact began to wind itself into a spiral. The tendency for the netting to sag and adjacent buoyancies to come in contact was noticed earlier when the net was towed away from the ship and then cast free. It can always be prevented by maintaining a pull on one end of the net. The coil of netting with the oil trapped in one small area was then left to float free overnight guarded by the MFV Alison Jane.

The recovery operation was conducted the next day, 12th September, by first getting MFV Alison Jane to locate the join in the netting and to pull this join out of the spiral of collapsed net. The join was taken to Seaspring and ends of the net were transferred respectively to the port and starboard sides of the ship (Figure 3A). By putting the ship broadside to the wind (Figure 3B) it was possible to recover surplus net using the

hydraulic rollers whilst keeping the bulk of oil at the far end of the loop of net. The ship being subject more to the wind than the net kept a tension on the net, and this could then be retrieved on board using the hydraulic rollers. The bow thruster was used to hold the ship in the position shown in Figure 3B. If the bow thruster was not used Seaspring tended to turn so that she pointed into the wind (Figure 3A).

When almost all the net had been recovered the ship was driven slowly forward at about 0.5 knot when the remainder of the net plus the oil came against the side of the ship (Figure 3C). The recovery head of the Springsweep airlift recovery system was then put into the oil and the oil taken on board.

By turning the direction of the bow thruster to port, the jet of water from the bow thruster discharge could be used to open up the net (Figure 3D) and so help the oil migrate towards the Springsweep skimmer. This was done roughly every fifteen minutes.

When the last of the entrapped oil was taken on board, the end of the net secured on the port side was cast free and the remainder of the net was recovered on board.

During the recovery it was observed that quite substantial quantities of oil were carried by the net up to and over the rollers. The amount was estimated to be of the order of 1 tonne emulsion for the 500 m of net in contact with the majority of the oil. The ship's fire hose was used to wash the net; but, as the ship was always down wind, the washing procedure brought water and some oil onto the recovery crew. The fire hose was turned off eventually as it was more expedient to allow the occluded oil to come on board than to try and wash it off.

Emulsion Preparation

The emulsion was prepared by putting a delivery of 9.4 m^3 medium fuel oil onto about 2.3 m^3 of sea water already in a suitable ship's tank and mixing the contents while further sea water was added slowly. In addition to using the Framo pump, the contents were recirculated using the ship's cargo pumps for 7.5 h until it was judged that the viscosity of the mixture had increased to about 8,000 mPa s and the flow through the cargo pump was becoming viscosity-limited. The Framo pump was run concurrently with the cargo pump and then for a further hour (total of 8.5 h) to produce an emulsion with about 60% water and with a viscosity of about 10,000 mPa s at a shear rate of 10 s^{-1} . The Framo TK-5 pump was subsequently run for a further 5 hours before the first release of oil to ensure that the contents of the tank were well mixed and to increase further the viscosity of the emulsion (Table 2).

Oil Recovery

The emulsion was recovered using the airlift components of the Springsweep oil recovery system and discharging the emulsion and free water into No. 2 starboard tank. A Hiab crane placed the 150 mm dia recovery hose with the skimmer head into the open tail of the net resting against the side of the ship.

The initial impression was that the layer of oil was possibly 25 cm thick at the back of the net and that the skimmer was almost totally immersed in oil so that the air flow, which is essential for efficient recovery, was being restricted. The time to partially fill the collection hopper (2.2 m^3 maximum capacity) was set at four minutes and a three-minute interval was used for the pressurised discharge. The oil recovery was

completed in about 2 hours.

The fluids recovered into No. 2 starboard tank were allowed to settle for 3 hours after which the water under the emulsion was pumped out. The initial dip of the tank indicated an apparent emulsion content of about 25 tonnes which was more than put out on the sea the previous day. Consequently, further pumping of settled water was carried out after the emulsion had stood for 15 days. The volume of the emulsion in the tank was then estimated as 20.0 tonnes.

RESULTS

The quantities of emulsion discharged and the quantities recovered together with the characteristics of the emulsion are summarised in Table 2. Subsequently the recovered oil was examined for viscosity under a range of shear rates using two viscometers and with the sample thermostatted at 17°C. The results obtained are given in Table 3.

TABLE 2. - Emulsion Discharge/Recovery Characteristics

	Discharge 3rd Sept	Discharge 11th Sept
<u>Quantity of Emulsion Released, tonnes</u>	5.0	21.5
Viscosity Dynamic** mPa s 17°C	65,000	71,100
Water Content % wt	51.0	59.0
Asphaltene Content of Medium Fuel Oil, % wt	3.3	3.3
<u>Quantity of Emulsion Recovered</u>		
On net, tonnes	1 (estimated)	1 (estimated)
By Springsweep Airlift Pump, tonnes	nil*	20.0 (15.7)***
Viscosity Dynamic** mPa s 17°C	-	73,700
Water Content % wt	-	67.9

* Although no oil was recovered about 3.5 tonnes was corralled but subsequently lost (except for 1 tonne adhering to the net)

** Viscometers UK Ltd type UKLV 8.

*** The observed 20 tonnes recovered with 67.9% water corresponds to only 15.7 tonnes of discharged emulsion containing 59% water.

TABLE 3. - Viscosity of Recovered Emulsion

Shear Rate (sec ⁻¹)	Viscosity mPa s at 17°C
0.2*	80,000
2.5**	18,000
10.8**	12,000
26.8**	9,000

* Viscometers UK Ltd type UKLV 8

** Ferranti Portable viscometer type VM

DISCUSSION AND CONCLUSIONS

The trials are considered to have been very successful and when assessed together with the earlier trials constitute sufficient work to show that nets are an attractive way to recover viscous oils at sea. Indeed nets are the only system ever tested by WSL where as much as 73% of the oil spilt has been recovered. Trials with other booms and skimmers have usually resulted in very much smaller percentages of oil recovery and in many trials no recovery at all has been possible. The other great advantage of nets is that they can be taken to sea and put out by small fishing vessels; each boat putting out by hand perhaps only 500 m of the net stored on deck.

The subsequent encirclement of oil, however, does require the use of a 500 hp or more powerful vessel; and the recovery operation would require the use of a small coastal tanker with a bow thrust facility for low speed manoeuvring.

Deployment and Recovery

The preliminary trials with the net conducted in July showed that launching the net from a vessel was easy provided that certain basic rules are followed, viz:

- (1) For hand launching the net needs to be on deck.
- (2) The vessel needs to be down wind of the net being launched, because the vessel is affected more by the wind than the net. The net can be launched into the wind however, provided it is pulled away by a second vessel.
- (3) Six men are needed to cast a 500 m net by hand which should take about 30-60 minutes depending on the weather and how many repairs are required.

The lengths of net can be joined together very easily, but lacing the net is time consuming. Although aluminium alloy sliding connectors were not used for the WSL trials they are used extensively with several impervious boom systems and would have enabled the join to have been made more easily. The fishing vessel, having a low free board, was used to lift short lengths of the boom out of the water for repairs to loose poles and it is clear that there would be no difficulty in joining various lengths of net together. The concept of lacing the ends together worked, but under tension gaps appeared and allowed oil to leak through. It was also a relatively slow operation as first the respective bolt ropes had to be shackled together before the nets could be laced up.

The recovery of the net is harder than deployment and can only be conducted with the assistance of a specially designed hydraulic roller. During the trials, net recovery was conducted in winds up to 25 knots where the drift of the recovery vessel was possibly 0.5 knot through the water and considerable tension was created in the net. The bow thruster when properly applied could be used to stop the drift temporarily to enable the net to be recovered. The ship has to be held such that the net coming on board is at right angles to the net roller. The incorrect use of the bow thrust unit to stop the drift would alter the position of the net in relation to the roller and cause the net to slide to one side. The watch officer on the ship's bridge needed to balance the position of the ship in relation to the incoming net. It was found useful to have a direct telephone link between the operator of the hydraulic rollers and the bridge. On another occasion the bow thrust controls were switched to the

bow of the ship where the co-ordinator of the recovery operation could take overall control of the ship.

When the net comes on board considerable quantities of water and oil are carried over the rollers, and the recovery crew handling the net need protective clothing. It was found relatively easy on Seaspring to feed the net straight into the hold from the hydraulic roller mounted on the side of the hatch coaming. Two men on a narrow walkway then flaked out the incoming net so that it laid on the floor of the hold. It was easy to stack 500 m in this way; but, further net would have made the stack more than 2 m high and the stack would have become unstable. The technique used during the trial was to return relatively clean net to the ISO container on the deck and to feed oily net into the hold where the oil could be collected on absorbent material placed around the stack.

Stacking the net into the ISO container was slow as the crew had to climb onto the net as it was laid out in flakes. Again the stack became unstable as the height increased and poles would tend to slide to one side. Mounting the hydraulic roller above the container door enabled the net to be lifted above the ISO container and made it somewhat easier to stack. However the flakes of net had to be carried to the back of the box by hand. Four men were needed in the box to stack the net, it was possible to put the 500 m length into the space provided attention was paid to careful stowing so that each buoyancy unit fitted snugly into the layer of net below.

Sweeping for Oil Recovery

The concept of corraling was foreseen to involve the encirclement of the spill by the net boom formed from short lengths joined together, after having been placed more or less in the appropriate position. However, the ease with which the kilometre length of boom was towed by Seaspring and Alison Jane, and especially the way in which Seaspring turned the net with Alison Jane attached to the end, suggests that it would be quite practical for two ships to tow a kilometre of net slowly and sweep an area of the sea until the quantity of oil in the curvature of the net reached several hundred tonnes, or oil started to escape from the net. Certainly the 1 km of net used in the present trial was unnecessarily long for the 21.5 tonnes of emulsion released.

The preliminary test, where Alison Jane towed a 500 m length of net and circled it without assistance from another ship, resulted in most of the oil being trapped. The free end of the net tended to follow the towing vessel and it was difficult for Alison Jane to retrieve the free end. It was considered from this exercise that encircling the oil would have been easier with a vessel at each end of the net.

The importance of aerial observation was ably demonstrated during the trial. Without this visual observation it would be difficult to be certain as to how effective is the sweeping exercise. Certainly without an aerial observer, little oil would have been surrounded by Alison Jane working with only 500 m of net.

When the net is in the shape of a U and being pulled by two vessels, it is essential that each vessel exerts a similar pull as it is easy for the stronger vessel to pull the smaller craft backwards with the net turning around an imaginary giant pulley wheel in the sea. Manoeuvres need to be carried out when the tension in the net is allowed to fall by one vessel stopping and allowing the other to turn.

When the tension is reduced the net slowly collapses and the buoyancy

units come into contact with each other. Although the height of the net between the poles falls there is no evidence that oil escapes over the sagged net. However, if a pole becomes disconnected, then the net does sag badly and the top edge can touch the sea to allow a possible loss of oil.

When left overnight with oil trapped within a circle much of the net became badly snagged with poles caught on the floats from adjacent or adjoining boom. In the absence of a thick layer of oil to keep any of the net apart the wall of the circle collapses to form a long double line of netting which then proceeds to curl up to form a spiral. It was found prudent to always keep some tension on the net to prevent spirals of collapsed net being formed; as, once one wall was in contact with its neighbour, damage could be caused by the ends of poles snagging in the net.

Recovery of Oil

The recovery of oil was probably the most straightforward of all the operations as once the net is alongside the recovery vessel it is relatively simple to lower one of a number of different skimmers into the oil. WSL successfully used the Springsweep airlift pump but satisfactory results would be expected from other different skimmers, such as those employing the screw pump principle, capable of lifting the corralled viscous oil on board.

Cleaning the Net

After an operational recovery of oil at sea, the net would be expected to be heavily soiled and not worth the cost of cleaning. It was found during the WSL trial that the use of water from the ship's fire hose was not very effective and there was insufficient time and resources to effectively operate a high pressure water wash system when the net was being hauled back on board. To install a high pressure water wash system at the point where the net comes on board would require very careful planning and would almost certainly interfere with the recovery operation.

The use of dispersants removed the free oil left on the net but did not clean off any of the oil entrained within the fibres of the woven net, consequently the used net appeared black and was unpleasant to handle. However, that which was only lightly oiled was salvaged and repaired, and can now be used again to meet possible operational and training needs.

The majority of the poles, buoyancy and lead weights taken off the net which was destroyed can be reused after washing in solvent.

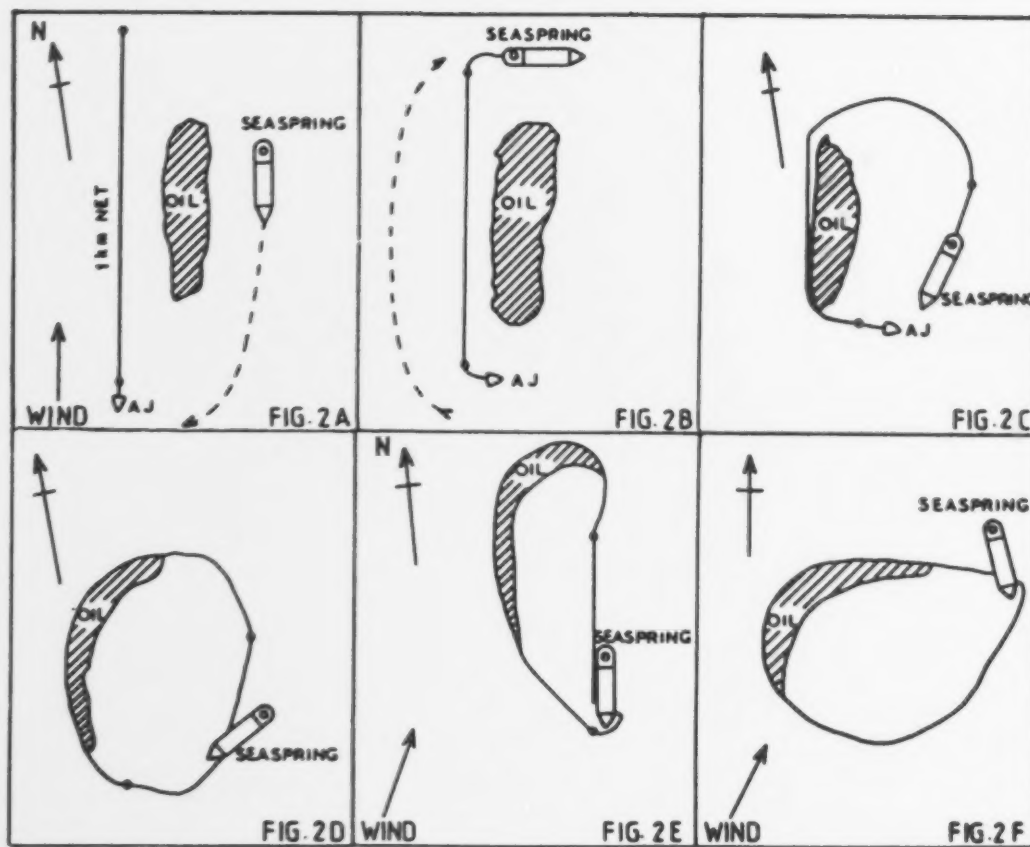
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1. Morris, P.R. and Thomas, D. The West Netting System for Inshore and Beach Protection Use. Stevenage: Warren Spring Laboratory, 1983, Report No. LR 453 (OP).
2. Thomas, D. and Morris, P.R. The West Netting System for the Recovery of Semi-Solid Oils. Sixth Arctic Marine Oil Spill Conference, Edmonton, Canada, 1983.



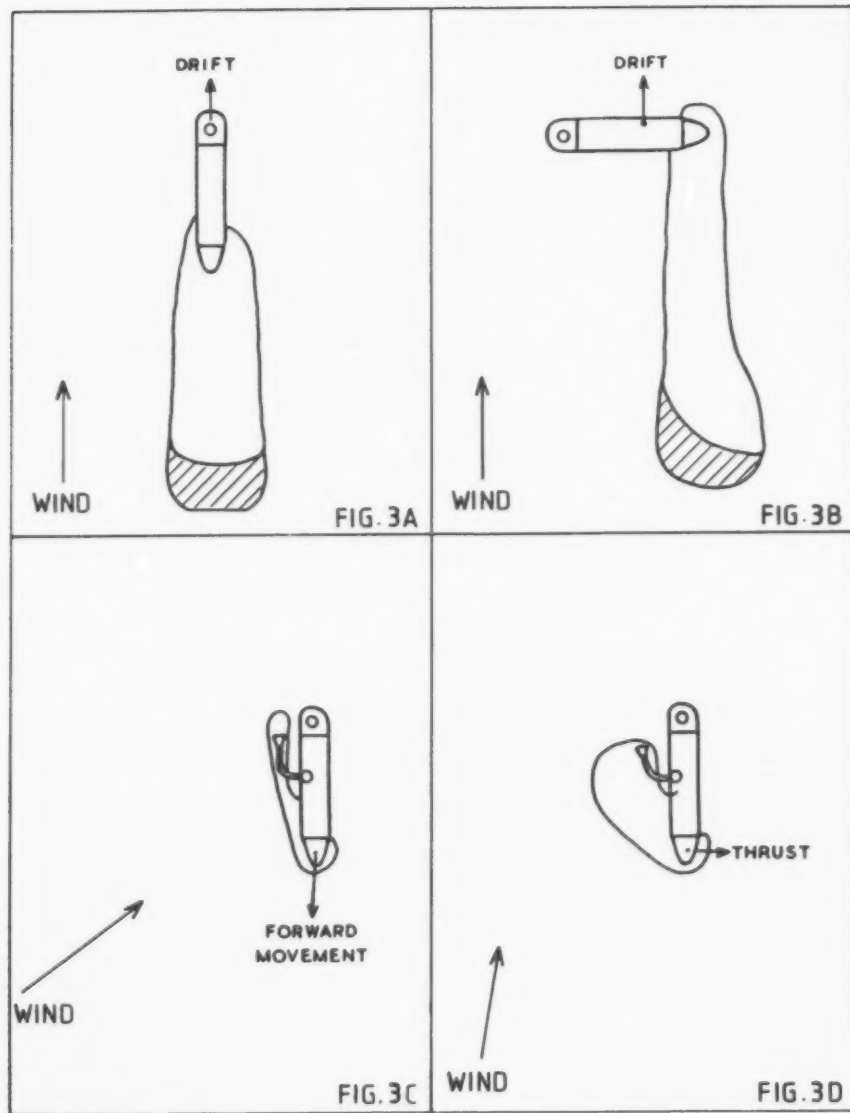
FIG.1 CLOSE-UP OF NETTING

(Pore dia ca 1mm)



17319

FIG. 2 SEQUENCE OF CORRALING MANOEUVRES.
11th SEPT



17312

FIG. 3 SEQUENCE OF RECOVERY OPERATIONS, 12 th. SEPT.

THE USE OF EMULSION INHIBITORS TO CONTROL OFFSHORE OIL SPILLS: PART 2

by

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INTRODUCTION

Preliminary results of a study to assess oil spill chemicals that inhibit emulsification were presented at the 1985 AMOP Conference. This paper covers the remainder of the study (completion of the small-scale effectiveness testing, dispersant effectiveness tests and meso-scale tank tests).

SMALL-SCALE EFFECTIVENESS TESTING

Purpose

The purpose of this phase of the study was to evaluate the emulsion-inhibiting performance of the Brand S surfactant in a larger scale test apparatus over longer time periods than the shaker system reported in the proceedings of the 1985 AMOP Conference. In addition the purpose was to assess the effect of the chemical on the competitive nature of emulsification and dispersion. Oil type, weathering, surfactant concentration, temperature, mixing energy, slick thickness and method of surfactant application were the experimental variables of the study.

Methods

Apparatus. This testing was conducted in a 42x42x42 cm tank filled to a depth of 20 cm with 34 L of water (Plate 1) and fitted with a variable-speed, vertically oscillating hoop to generate radial waves. The tank contained a 42-cm diameter circular plexiglass insert that served to reflect the waves and thus hold the test oil in the centre of the tank to minimize edge effects.

Grab samples of emulsion were taken periodically and analysed for oil content by a spectrophotometric technique. Dispersed oil concentrations were analysed similarly.

Test Matrix. The test programme included the following matrix of variables:

- * two water salinities (fresh and 35 ppt)
- * three temperatures (0°C, 10°C, and 20°C)
- * three states of weathering (fresh crude, 1 and 5 days exposure)
- * two oil slick thicknesses (1.5 mm and 5 mm)
- * two levels of mixing energy of the hoop apparatus (150 rpm and 220 rpm)
- * two crude oils: Alberta Sweet Mixed Blend (substituted for Kuwait) and Avalon J-34 crude oil (see Tables 1 and 2)
- * four surfactant-to-oil ratios: (0:10,000, 1:5000, 1:1000)
- * and three methods of chemical application: pre-mixed, dropwise and sprayed-on.



PLATE I - HOOP TANK APPARATUS

TABLE 1: Physical Properties of the Alberta Sweet Mix Blend Crude Oil

Mass Evaporated (%)	0	20.5	26.7	273		
Evaporative Exposure (Θ)	0	5.1×10^4	2.5×10^5			
Temperature ($^{\circ}\text{C}$)	20	10	0	20	10	0
Oil Density (g/cm^3)	0.8415	0.8760	0.8885	0.8421	0.8857	0.8977
Oil/Water Interfacial Tension (mN/m)	26.5	26.4	27.0	24.4	*	*
Oil Viscosity (mPas)	4.8	7.8	15.3	68.4	312	376400
Oil Pour Point ($^{\circ}\text{C}$)		-4			19	22
				328	147200	446000

* Oil was too viscous for interfacial tension measurements.

Table 2: Physical Properties of the Avalon J-34 Crude Oil

Mass Evaporated (%)	0	10.4	11.9
Evaporative Exposure (Θ)	0	8.1×10^4	3.6×10^5
Temperature ($^{\circ}\text{C}$)	$\frac{20}{10}$ 0	$\frac{20}{10}$ 0	$\frac{20}{10}$ 0
Oil Density (g/cm^3)	0.8753 0.8885 0.8893	0.8974 0.9081 0.9102	0.9054 0.9156 0.9181
Oil/Water Interfacial Tension (mN/m)	28.7 34.5 *	31.8 * *	31.2 * *
Oil Viscosity (mPas)	39.6 173 268400	228 87200 480000	640 108000 1026000
Oil Pour Point ($^{\circ}\text{C}$)	21	24	25

Oil was too viscous for interfacial tension measurements.

Brand S, a commercial demulsifier which is manufactured in Europe was the surfactant used in these tests. It is non-ionic in nature, has a pour point below -10°C , a water solubility of less than 0.01% and a density of 1.02 g/ml at 20°C . Because it is highly viscous (dynamic viscosity of 1170 cP at 20°C) it was necessary to dilute the product 50% by volume with acetone in order to facilitate the use of a microlitre syringe to deliver the small volumes required in the tests.

Results and Discussion

The agitation of the surfactant/oil/water mixtures typically resulted in one of four possibilities depending on the experimental conditions. One was the formation of a viscous brown emulsion or "mousse", evident as a circular patch about 2 cm thick and 17 cm in diameter that floated at the water surface and resulted in little or no dispersion.

A second possibility was the total dispersion of the oil slick in the form of droplets with diameters much less than 1 mm. This made the water phase extremely cloudy and dark brown in colour or even black and opaque.

Third, was the formation of a weak, black-coloured emulsion having large (1 mm diameter) water droplets mixed throughout. These emulsions had viscosities only marginally greater than their parent oils, contained 20-70% by mass water and produced low dispersion concentrations.

Lastly, was the formation of non-coalescing "emulsion" globules on the surface which consisted of either pure oil (in those cases where the oil was below its pour point) a weak emulsion (20-70% by mass water content) or a viscous emulsion (75% by mass water or more). These ranged in size from 1-cm diameter globules to thick mats about 10 cm^2 in area.

Emulsification and Dispersion of Fresh Oil. Figure 1 shows the emulsion water content as a function of time for the Avalon J-34 oil (fresh). With no inhibitor present the oil rapidly takes up water, initially in the form of large (about 2 mm) droplets, to form a black lumpy emulsion. These large droplets appear to break down to smaller size ($<1\text{ mm}$) over a period of about an hour. After two hours the emulsion turns into the familiar, smooth, brown "mousse" surrounded by a thin ring of the black emulsion. The underside of the emulsion slick is distinctly hilly.

Addition of increasing concentrations of the Brand S inhibitor increasingly delays the onset of emulsion formation. As can be seen on Figure 1 an inhibitor concentration of 1:10,000 delays the onset of emulsification for 1 to 1.5 hours while the addition of 1 part inhibitor in 5,000 parts oil prevents the formation of the emulsion for the entire test period.

Figure 2 shows the dispersed oil concentrations, measured at the bottom of the tank (about 20 cm below the surface), for each of the three tests with the East Coast oil. It is evident that increasing concentrations of the inhibitor dramatically increase dispersed oil concentrations. Of equal interest is the effect of emulsification on dispersion. Comparing the curves of Figures 1 and 2 for the untreated oil indicates that as the emulsion ages and becomes more viscous (i.e., the water droplets get progressively smaller) the amount of dispersed oil decreases. This implies that the rate of dispersion is decreasing (assuming a constant rate of dispersed oil recoalescence). Over the 3 hour test the dispersed oil concentrations dropped from 150 ppm to about 50 ppm. The visible oil droplets were in the 1 to 5 mm size range. It should be noted that a homogeneously mixed oil concentration of about 4000 ppm would represent all the oil dispersed into the tank.

FIGURE 1 : EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

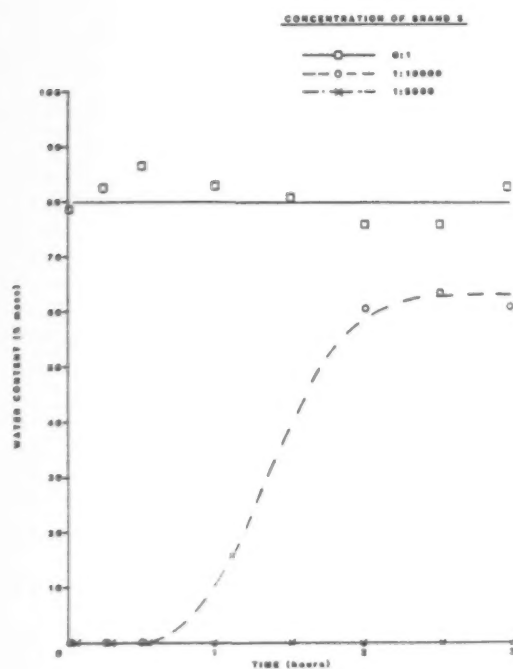


FIGURE 2 : DISPERSION VS TIME (FRESH J-34)

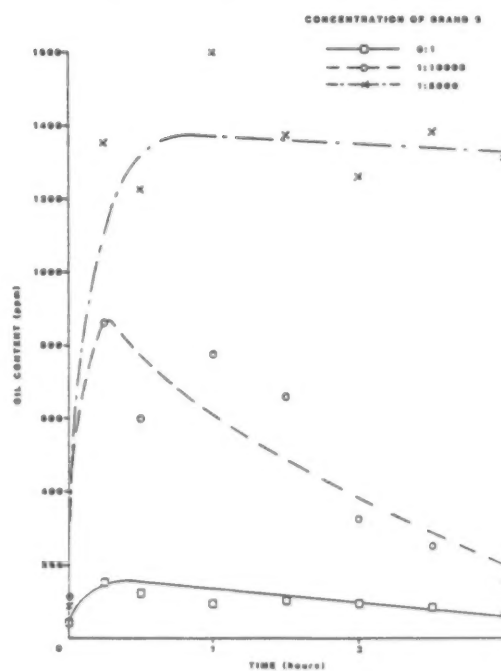


FIGURE 3 : EMULSIFICATION VS TIME (FRESH ASMB AT 20°C)

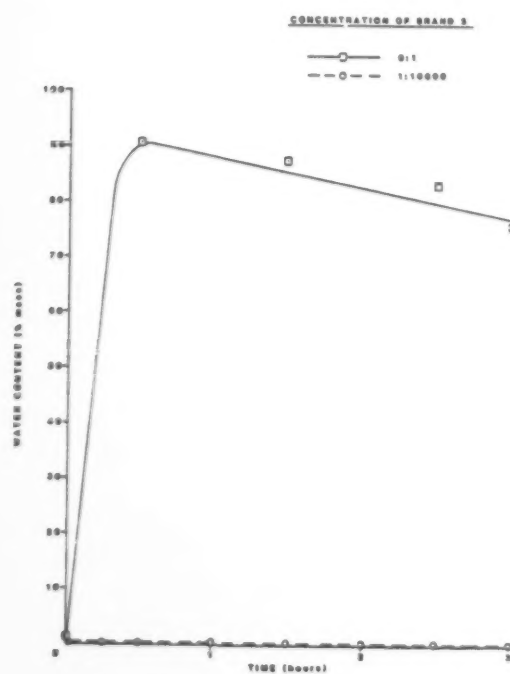
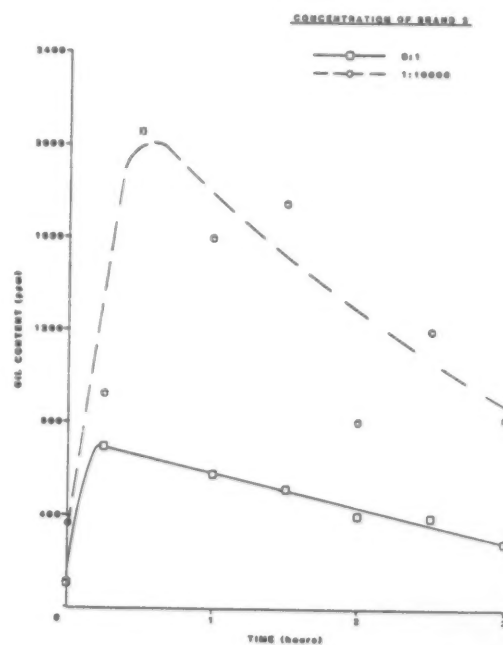


FIGURE 4 : DISPERSION VS TIME (FRESH ASMB)



The competitive nature of emulsification and dispersion is more dramatically demonstrated in comparing the results, on Figures 1 and 2, for the test with 1 part inhibitor in 10,000 parts oil. Initially (prior to emulsification) the dispersed oil concentration level rose rapidly to 900 ppm. After about an hour it began to fall. At the end of the 3-hour test the oil concentration had dropped to 150 ppm. Dispersed oil droplet sizes for the dosed oils were much less than 1 mm in size.

Figure 3 shows similar results for tests run with the Alberta Sweet Mixed Blend (ASMB) crude oil. Addition of 1 part inhibitor to 10,000 parts oil results in the prevention of emulsification over the three hour test. In this case almost all of the oil was immediately dispersed as fine ($\ll 1$ mm) droplets yielding a measured concentration of 2000 ppm).

Figure 4 shows that the dispersion concentration for the inhibitor-free oil peaked at about 700 ppm. The droplet sizes were somewhat less than 1 mm. The dispersed oil concentration decreased to 250 ppm after 3 hours, as the oil emulsified. The higher oil-in-water concentrations and smaller droplet sizes for the ASMB crude as compared to the J-34 crude can be attributed to the ASMB crude's lower viscosity and interfacial tension.

Effects of Oil Weathering on Surfactant Performance. Figure 5 shows that the emulsion inhibiting performance of the surfactant is affected by oil weathering. With fresh J-34 oil a surfactant-to-oil ratio of 1:10,000 inhibits emulsification for an hour. With the same oil artificially weathered to an evaporative exposure of 8×10^4 (24 hours) a dosage of 1:5000 is required to inhibit emulsification over the entire test period. The same oil weathered to an evaporative exposure of 3.6×10^5 (121 hours) requires a dosage of 1:1000 to inhibit emulsification. It is likely that this effect is related to an increase in bulk oil viscosity rather than an increase in the relative concentration of natural emulsion-stabilizing compounds in the weathered oil. The dose of surfactant required to inhibit emulsification increases by an order of magnitude over the range of weathering, as does the oil viscosity, while the relative concentration of non-volatile components increases only slightly due to the 12% mass loss to evaporation.

Figure 6 shows the effects of oil weathering on the dispersed oil concentration beneath the dosed slick. As the slick becomes more weathered higher concentrations of surfactant are required to achieve the same dispersion. The relationship is different than for emulsion inhibition: dosages of 1:10,000 for fresh and 24 hour weathered and 1:5000 for 121 hour weathered oil achieve similar dispersions. This indicates that factors other than just oil viscosity play a role in determining the dispersion rate enhancement effect of the surfactant. Reduced interfacial tension is known to greatly enhance dispersion.

Figure 7 shows the effects of weathering on the performance of the surfactant in inhibiting emulsification with Alberta Sweet Mixed Blend crude oil. Effective dose rates were 1:10,000 for fresh and 24 hour weathered ($\Theta = 5 \times 10^4$) and 1:5000 for 121 hour weathered ($\Theta = 2.6 \times 10^5$). The 1:5000 dose for the 121 hour weathered crude initially seemed to be insufficient and a black emulsion began to form, however after 1.5 hours this had completely dispersed. As with the J-34 oil, the oil viscosity seems to be the dominating factor in controlling surfactant performance. In fact, the 121 hour weathered ASMB (with a viscosity of 330 mPas at 20°C) required the same dose rate as 24 hour weathered J-34 (230 mPas at 20°C) to inhibit emulsification.

Figure 8 shows the dispersed oil concentrations for the runs shown on Figure 7. Since a concentration of about 4,000 ppm represents all the oil homogeneously mixed in the 34 L tank, it is clear that the surfactant, in the case of ASMB, shifts the equilibrium from

FIGURE 5: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (J-34 AT 20°C)

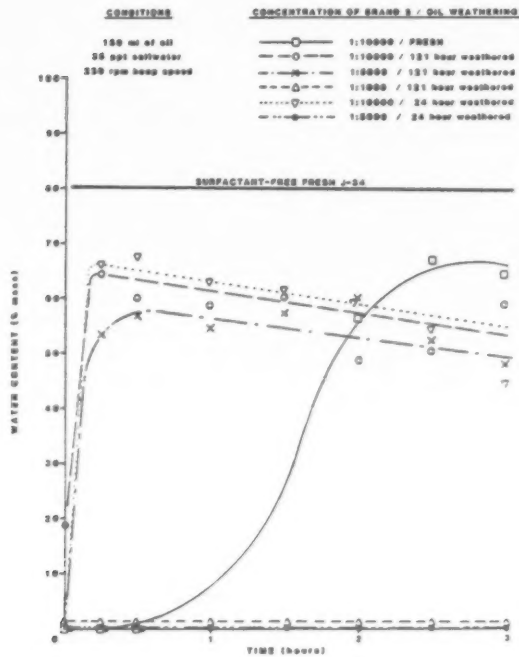


FIGURE 6: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (J-34 AT 20°C)

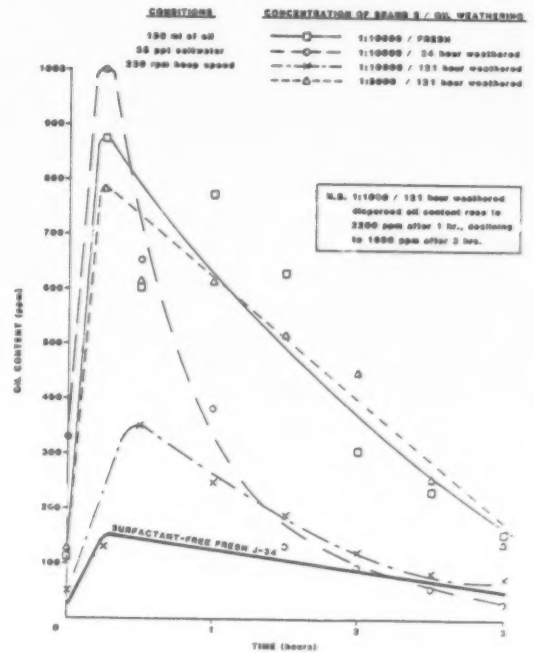


FIGURE 7: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (ASMB AT 20°C)

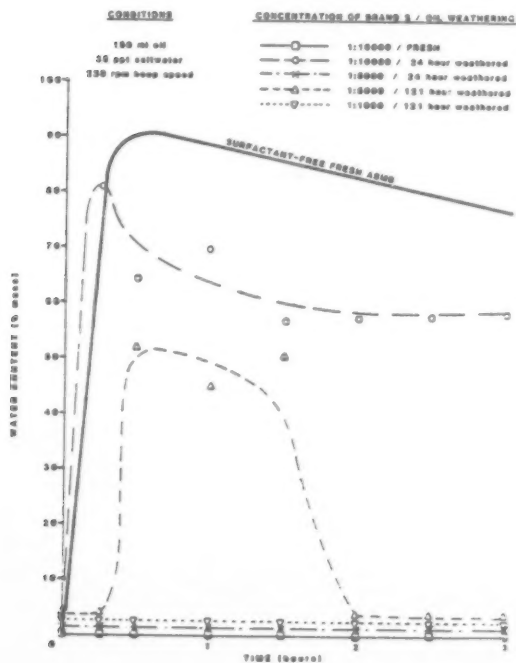
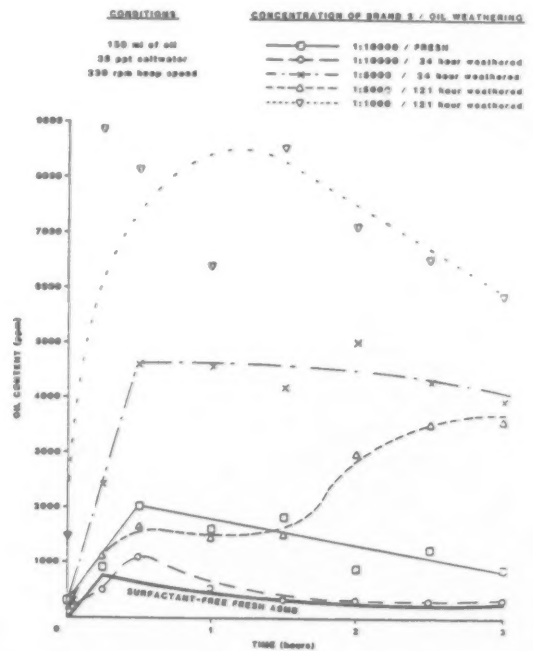


FIGURE 8: EFFECT OF WEATHERING ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (ASMB AT 20°C)



emulsification to complete dispersion for doses of 1:5000 for 24 hour and 121 hour weathered and 1:1000 for 121 hour weathered crude oil. Lower concentrations (above the minimum required) inhibit emulsification without resulting in complete dispersion (e.g., 1:10,000 in fresh oil).

Effects of Temperature on Surfactant Performance. Figure 9 shows the effect of temperature on the performance of the surfactant in inhibiting emulsification for fresh and weathered J-34 oil. As the temperature decreases, higher concentrations of surfactant are required to prevent emulsification. For example, fresh J-34 requires 1:10,000 at 20°C, and 1:5000 at 10°C. Similarly for 24 hour weathered J-34, 1:5000 is required at 20°C and 1:1000 at 10°C. At 20°C 1:1000 easily prevents emulsification of the 121 hour aged oil while at 10°C 1:1000 barely inhibits emulsion formation. Neither weathered oil formed a tightly bound emulsion at 10°C.

It is interesting to note that the results of Figure 9 appear to show that the chemical was effective with J-34 oil at 0°C, in that no emulsion was formed. The fact is that at this temperature, which is 20°C below the oil's pour point, the oil formed immediately into 1-4 cm diameter balls and remained in this form throughout the test period.

The above results confirm that oil viscosity plays a key role in determining surfactant performance; for the fresh oil case a drop in temperature from 20° to 10°C results in a 4 fold increase in viscosity and a doubling of the surfactant dose required to prevent emulsification.

As noted, pour point also plays a significant role in emulsification. Once the temperature drops 10 to 15°C below the pour point the oil "gels" even at the relatively high shear rates in the hoop tank. This greatly inhibits the incorporation of water droplets into the oil as well as the breakdown of large drops into small drops. As the temperature drops to 20°C below the pour point the oil no longer forms a slick or coherent mass; it is fragmented into solid-like balls which do not coalesce, disperse into smaller droplets or take up water.

Figure 10 shows the effect of temperature on dispersed oil concentrations beneath dosed, fresh and weathered J-34 oil. In comparison with Figure 6 a drop in temperature from 20°C to 10°C approximately halves the dispersed oil concentration.

Table 3 presents the results obtained for similar runs with the ASMB crude oil. In this case, because ASMB is less viscous than J-34, the surfactant was more effective with the weathered oils at 10°C. In the case of the 121-hour weathered oil at 10°C, the temperature was far enough below the pour point (22°C) that the oil was beginning to exhibit "gel"-like behaviour.

Dispersed oil concentrations were considerably higher for the ASMB than for the J-34 oil, again because of the ASMB oil's lower viscosity. A concentration greater than 4000 ppm indicates complete dispersion of the oil sample.

Combined Effect of Weathering and Temperature. Table 4 summarizes the minimum surfactant dosage required to prevent emulsification for both oils as a function of temperature and weathering for the previously discussed tests.

Effect of Slick Thickness on Surfactant Performance. Figures 11 and 12 illustrate the effect of slick thickness (150 ml = 5 mm vs 50 ml = 1.5 mm) on the emulsification and dispersion of dosed Avalon J-34 crude oil. At a surfactant concentration of 1:10000 the thinner slick dispersed almost completely while the thicker slick gradually developed from 5 mm globules into a 60% water-in-oil emulsion over 2 hours. At 1:5000 both slicks dispersed rapidly; the 1.5 mm slick dispersed as very small droplets ($\ll 1$ mm) while the 5 mm slick dispersion contained many larger droplets (≈ 1 mm).

FIGURE 9: EFFECT OF TEMPERATURE ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (J-34)

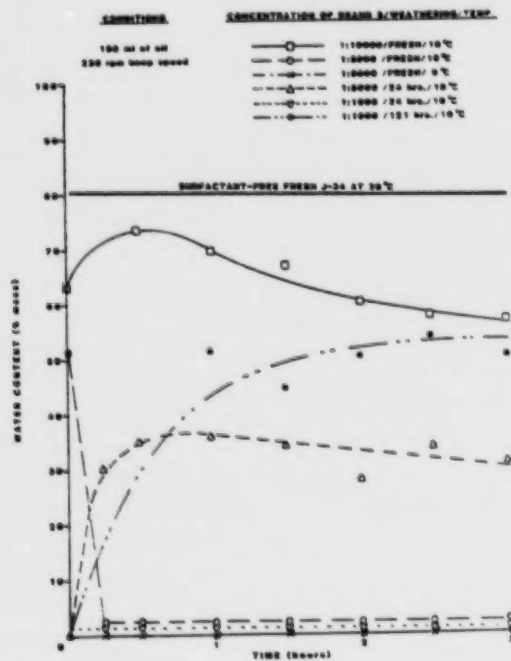


FIGURE 10: EFFECT OF TEMPERATURE ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (J-34)

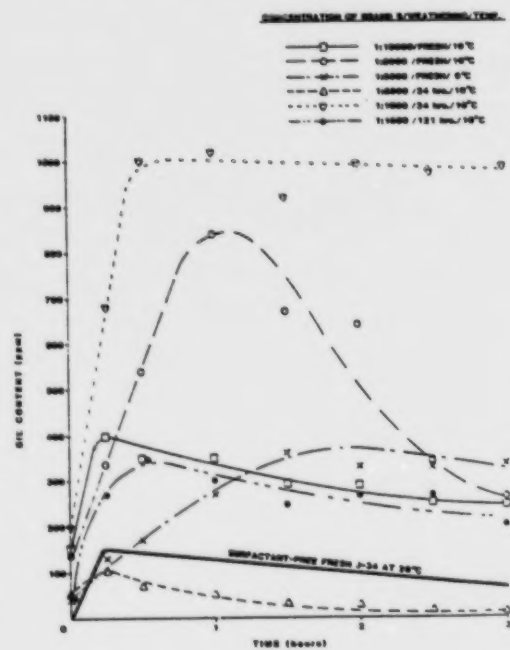


FIGURE 11: EFFECT OF SLICK THICKNESS ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

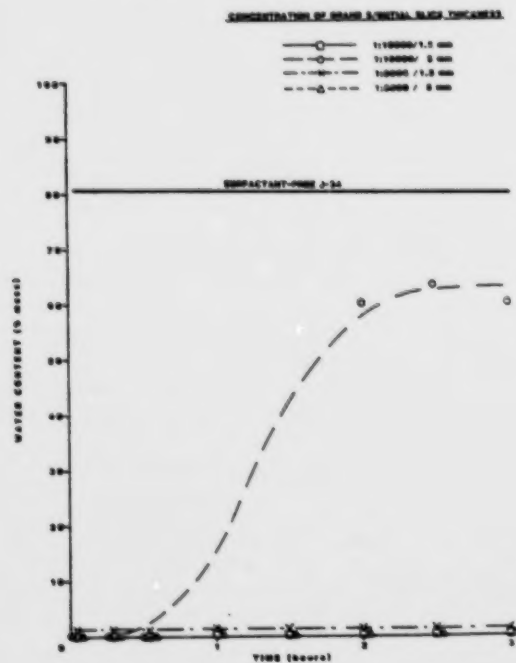


FIGURE 12: EFFECT OF SLICK THICKNESS ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (FRESH J-34 AT 20°C)

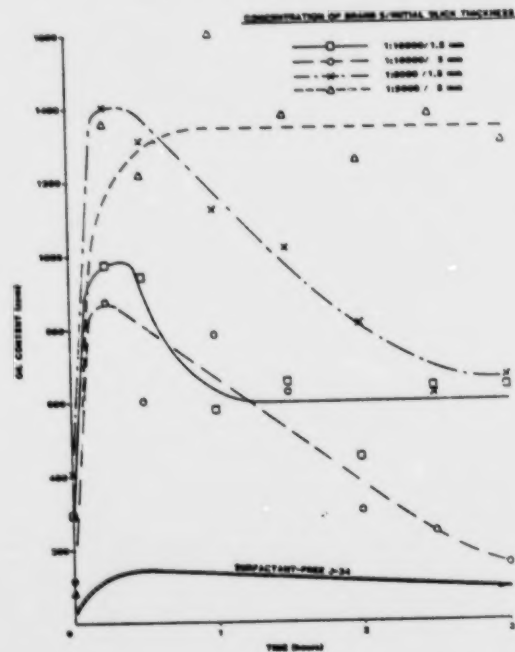


TABLE 3

Effects of Temperature on Surfactant Performance: ASMB

Temperature (°C)	Evaporative Exposure (°)	Dose of Surfactant (vol:vol)	Final Water Content (% mass)	Final Dispersed Oil Concentration (ppm)
20	0	0:1	80	90
	0	1:10,000	0	800
	5x10 ⁴	1:10,000	60	140
	5x10 ⁴	1:5000	0	4200*
	2.6x10 ⁵	1:5000	0	3500
	2.6x10 ⁵	1:1000	0	6000*
10	0	1:5000	0	5000*
	5x10 ⁴	1:1000	0	2500
	2.6x10 ⁵	1:1000	40	1300
0	0	1:1000	0	4000*

* oil completely dispersed

TABLE 4: A Summary of the Lowest Feasible Concentration of Brand S Required to Inhibit Emulsification Under Various Conditions

Oil Type	Temperature	Fresh Oil	24 hour weathering	121 hour weathering
Avalon J-34 Crude Oil	20°C	1:5000	1:5000	1:1000
	10°C	1:1000	Marginal @ 1:1000	Failed @ 1:1000
	0°C	oil gelled into balls		
Alberta Sweet Mixed Blend Crude Oil	20°C	1:10000	1:5000	1:1000
	10°C	1:5000	1:1000	marginal @ 1:1000
	0°C	1:1000	D.N.T.	D.N.T.

D.N.T. = did not test

Effect of Mixing Energy on Surfactant Performance. Figure 13 shows the effect of mixing energy on emulsification and the performance of the surfactant. At the lower hoop oscillation rate surfactant free oil incorporates water as rapidly as at the higher rate but the water drops are much larger at the lower rate than at the higher (1 to 10 mm diameter as opposed to < 1 mm). The emulsion that was formed at the lower mixing energy separated once it was removed from the test tank.

As shown in Figure 13, surfactant performance (at 1:10000) is better at the higher mixing energy level than at the lower, but that the final water content of the emulsion is the same for both. The results at 1:5000 are unusual, but duplicate runs done at 1:5000 at 150 rpm indicated that the equilibrium water content is zero and that the rise in water content shown on Figure 13 is an anomaly.

The effect of mixing energy on dispersion is quite dramatic; a decrease in hoop oscillation rate from 220 to 150 rpm results in almost an order of magnitude decrease in dispersed oil concentration (Figure 14). Two different energy types are required for dispersion, one to create droplets from a slick (in a range of sizes) and one to determine what percentage of these droplets remain dispersed and what percentage rise to recombine with the slick. Obviously the surfactant can only influence the first of these by reducing interfacial tensions and allowing more and smaller droplets to be produced per unit energy.

Surfactant Application Techniques. Figure 15 shows a comparison of surfactant application methods (premixed vs dropwise or sprayed). Premixed is the most efficient technique with dropwise addition being far superior to fine-mist addition.

Figure 16 shows the dispersion results for these same tests. Spraying as a fine mist is an inefficient method of surfactant delivery for the J-34 oil.

For fresh ASMB, however, both sprayed and dropwise addition at 1:5000 resulted in complete dispersion of the fresh oil at 20°C (Figure 17). The difference between the two oils is likely related to their pour points (21°C for J-34 vs -4°C for ASMB). The surfactant has difficulty penetrating and mixing with the J-34 while it mixes easily with the more fluid ASMB.

Comparison with Dispersants. Figures 18 and 19 show a comparison of the performance of Brand S vs Corexit 9527, a state-of-the-art oil spill dispersant. A premixed concentration of 1:5000 of Brand S resulted in complete dispersion of the oil whereas the 1:5000 premixed 9527 formed a weak emulsion containing 1 mm diameter water droplets. It is not surprising that 9527 does have a slight emulsion inhibiting effect since one of its active ingredients is sodium dioctyl sulfosuccinate (Wells et al 1985) tested during the first phase of this study.

Figures 20 and 21 illustrate that salt content has no effect on the performance of the surfactant in inhibiting emulsification or in enhancing dispersion.

FIGURE 13: EFFECT OF MIXING ENERGY ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

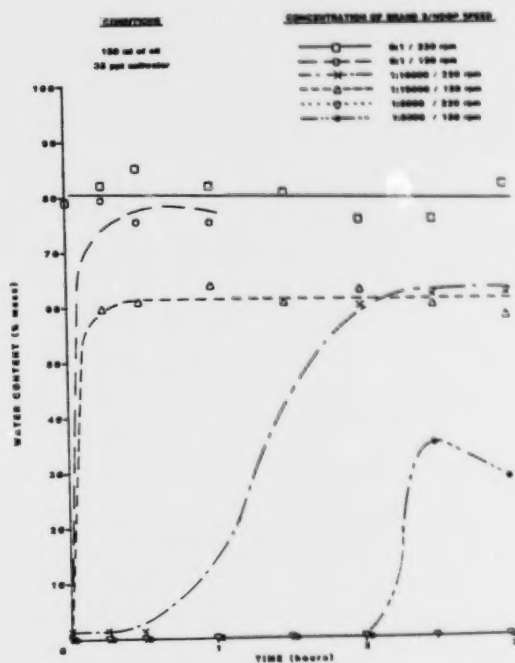


FIGURE 14: EFFECT OF MIXING ENERGY ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (FRESH J-34 AT 20°C)

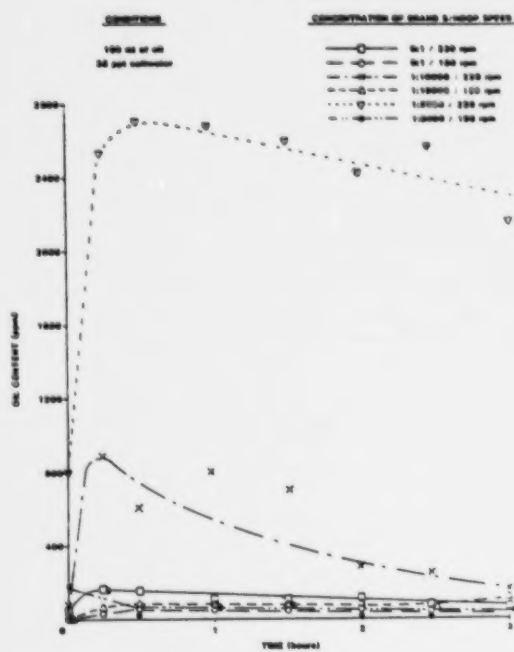


FIGURE 15: COMPARISON OF SURFACTANT APPLICATION METHODS
EMULSIFICATION VS TIME (J-34 AT 20°C)

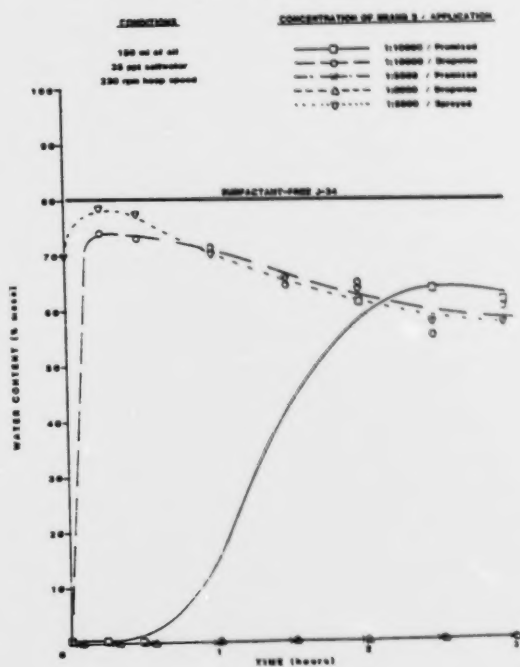


FIGURE 16: COMPARISON OF SURFACTANT APPLICATION METHODS
DISPERSION VS TIME (J-34 AT 20°C)

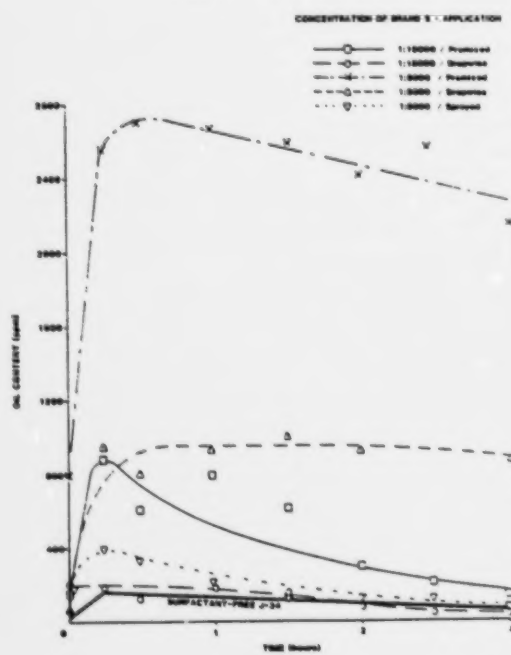


FIGURE 17: COMPARISON OF SURFACTANT APPLICATION METHODS
DISPERSION VS TIME (ASMB AT 20°C)

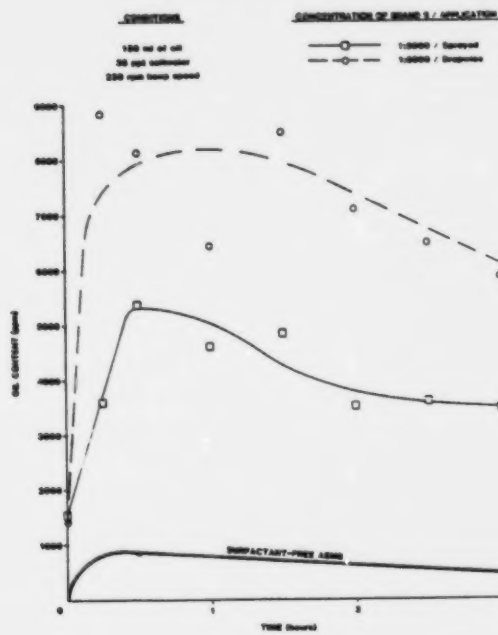


FIGURE 18: COMPARISON OF SURFACTANTS
EMULSIFICATION VS TIME (J-34 AT 20°C)

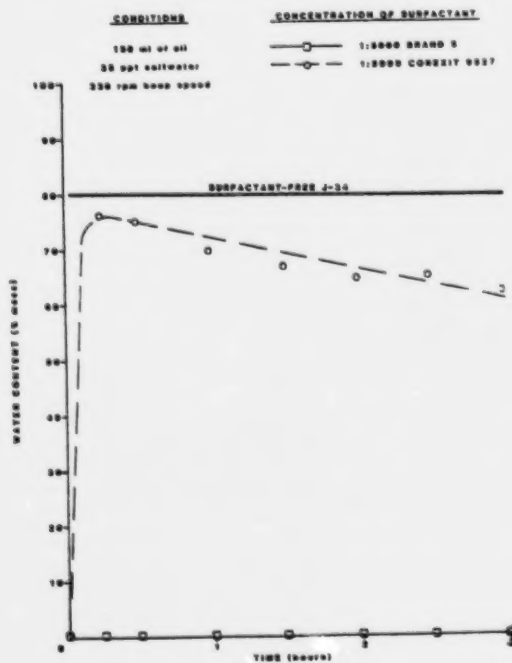


FIGURE 19: COMPARISON OF SURFACTANTS
DISPERSION VS TIME (J-34 AT 20°C)

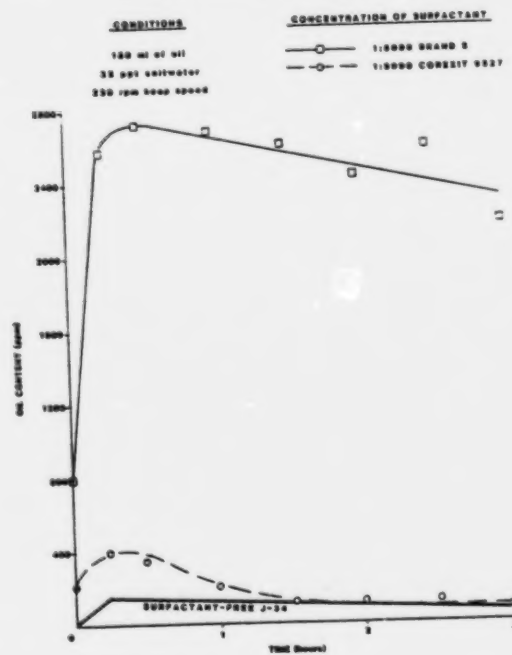


FIGURE 20: EFFECT OF WATER SALINITY ON SURFACTANT PERFORMANCE
EMULSIFICATION VS TIME (FRESH J-34 AT 20°C)

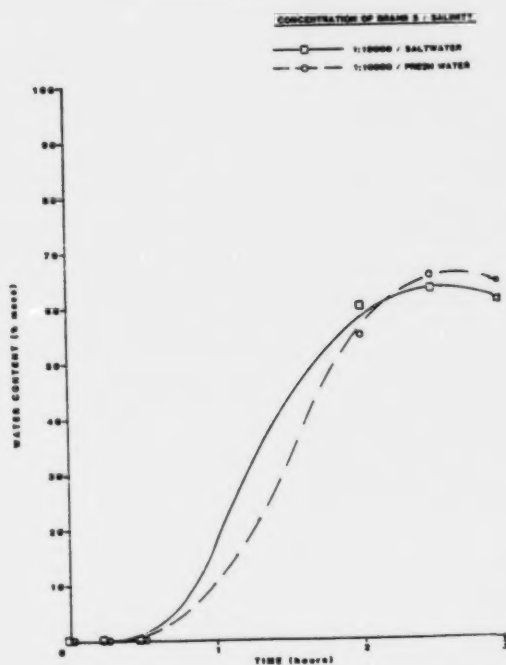
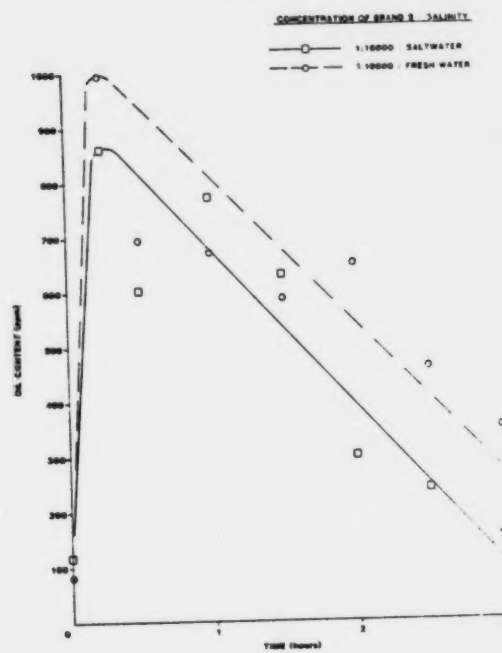


FIGURE 21: EFFECT OF WATER SALINITY ON SURFACTANT PERFORMANCE
DISPERSION VS TIME (FRESH J-34 AT 20°C)



DISPERSANT EFFECTIVENESS TESTING

Since the chosen emulsion inhibitor unexpectedly proved in the small-scale testing to significantly promote dispersion as well as inhibit emulsification it was decided to more fully test the effectiveness of the chemical as a dispersant.

Purpose

The goal of this phase of the study was to determine the effectiveness of Brand S as a dispersant and the effect of solvent and temperature on its performance.

Methods

The tests were conducted in an MNS dispersant effectiveness apparatus according to Environment Canada standard procedures (Environment Canada 1984) using EPS Standard ASMB crude oil. The tests were conducted in the cold room at Environment Canada's River Road Environmental Technology Centre.

The inhibitor was diluted 1:100 in solvent for most of the runs to make possible even, dropwise addition of small amounts of the chemical. Blanks (solvent only) were run to assess the effect of the solvent. Control runs were also performed with no inhibitor or solvent added. The test matrix included the following parameters:

- * four temperatures (0, 5, 10 and 15°C)
- * one energy level (30 cm H₂O pressure drop)
- * four inhibitor:oil ratios (1:500, 1:1000, 1:2000 and 1:4000)
- * four solvent types (neat, toluene, naptha and acetone)
- * two application methods (premixed or dropwise)

In addition two commercially available dispersants (Corexit 9527 and 9550) were tested under identical conditions (with dispersant:oil ratios of 1:20, 1:50 and 1:100) with and without preaddition of the inhibitor. These tests were conducted to determine if the inhibitor had any effect on conventional dispersant performance.

Results and Discussion

Table 5 shows the results of the tests at an inhibitor:oil ratio of 1:500. (Repeatability of the MNS test is within 5 percent.) The blanks to assess natural dispersion are shown at the far right; not shown are the solvent only blanks at 15°C which resulted in dispersions of 7.5, 10 and 9% respectively for toluene, naptha and acetone premixed with the oil at 1:5 (the volume of solvent used to get a 1:500 inhibitor-to-oil ratio).

The results show that at 10 and 15°C the inhibitor is a surprisingly effective dispersant; as the temperature decreases below 10°C, however, its effectiveness declines dramatically. In terms of application method and solvent, premixed/neat gives the best results. At 15°C 1:500 in toluene premixed seems to give a better result; this may be the result of an experimental error or a synergistic effect between the inhibitor and toluene (toluene alone at the same volume ratio does not increase dispersion). Experimental error is the most likely reason since the result is not repeated at 10°C. Runs using naptha as a solvent consistently yielded the poorest results.

Figures 22 and 23 show the effect of inhibitor dose on dispersion at 15°C and 10°C respectively. The curves for 15°C indicate that the inhibitor reaches a critical micelle concentration above which the addition of more surfactant has little or no further effect. At this temperature, at dose rates of 1:1000 or greater, there is little difference between premixed neat and dropwise addition in a solvent. At 10°C significant differences become apparent. The neat premixed case still seems to reach a critical micelle concentration but the solvent cases do not. Overall, dispersant efficiency at 10°C (neat, premixed) is only 2/3 that at 15°C. Tests at different doses were not conducted at lower temperatures since the inhibitor did not significantly promote dispersion at dose rates of 1:500 at 5°C and 0°C.

TABLE 5

DISPERSANT EFFECTIVENESS OF BRAND "S"
(Percent Dispersed)

I/O	1:500	1:500	1:500	1:500	1:500	1:500	1:500	1:500	1:500	blank
Solvent	neat	toluene	toluene	naptha	naptha	toluene	dropwise	dropwise	acetone	acetone
Application	premixed	premixed	dropwise	premixed	dropwise	dropwise	dropwise	dropwise	premixed	dropwise
Temperature (Deg C)										
0	3	4		3					3	3
5	9	8		7					4	4
10	48	35	33	26	15				8	6
15	68	79	69	46	52				61	10

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Notes: I/O is the inhibitor to oil ratio

Inhibitor was diluted 1 to 100 in the solvents

Premixed: oil and inhibitor are mixed together and then discharged onto the water surface

Dropwise: inhibitor is added to the oil surface in droplet form from an Eppendorf pipette

FIGURE 22: EFFECTIVENESS OF BRAND S AS A DISPERSANT AT 15°C

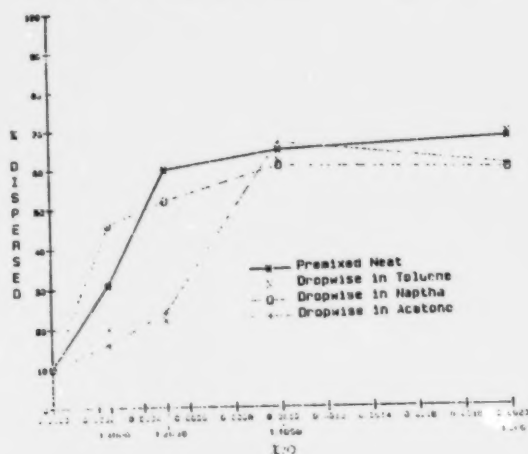


FIGURE 23: EFFECTIVENESS OF BRAND S AS A DISPERSANT AT 10°C

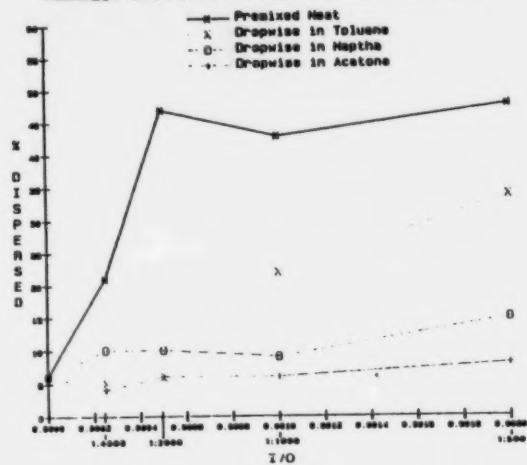


FIGURE 25: COMPARISON OF TEMPERATURE EFFECTS ON DISPERSANT EFFECTIVENESS

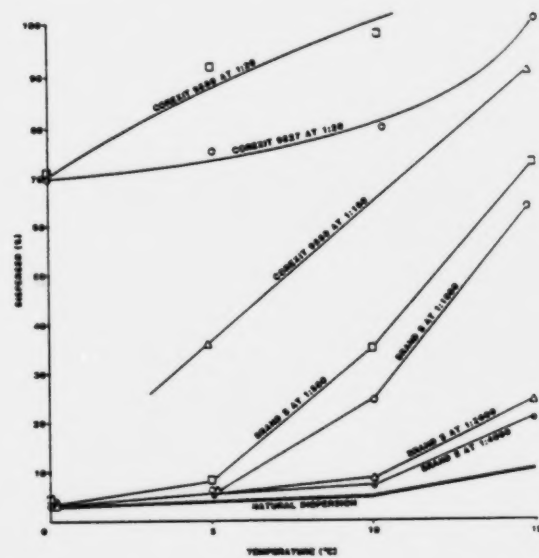


FIGURE 24: DISPERSANT EFFECTIVENESS OF BRAND S AT I/O = 1:500 AS A FUNCTION OF TEMPERATURE

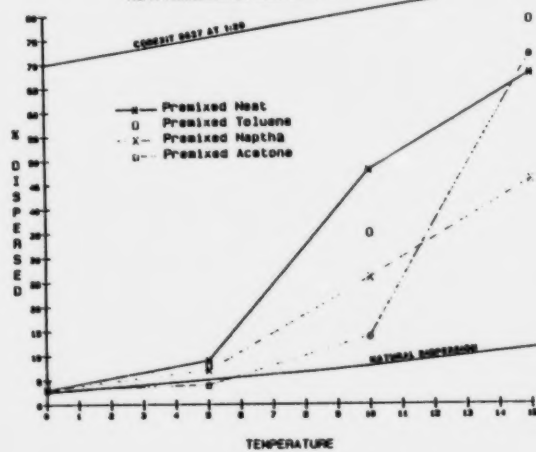


Figure 24 illustrates the effect of temperature on the enhancement of dispersion by Brand S. As with emulsion inhibition 10°C seems to be a critical temperature. Unlike emulsion inhibition the phenomenon cannot solely be linked with oil viscosity effects as evidenced by the different slopes of the dosed, natural dispersion curve vs the Corexit 9527 @ 1:20 curve, both of which rise only slightly with increasing temperature. It may be that the mobility of the surfactant in the oil is a contributing factor.

Figure 25 shows a comparison of temperature effects on dispersant effectiveness for Corexit 9527 at 1:20, Corexit 9550 at 1:20 and 1:100 and Brand S at 1:500, 1:1000, 1:2000 and 1:4000. All chemicals were added dropwise. For a given surfactant, as the concentration decreases, above the critical micelle concentration, the slope of the effectiveness vs temperature curve increases. This implies that the migration of surfactant molecules within the oil to freshly created interface as the oil droplets split may be limiting the effectiveness of the chemicals.

Tables 6 and 7 show the results of tests conducted to determine the effect of the inhibitor on conventional dispersant effectiveness. The presence of Brand S consistently resulted in a slight improvement in the effectiveness of Corexit 9527 and 9550 at all temperatures and concentrations tested.

TOXICITY TESTING

Brand S was subjected to the standard EPS toxicity test for dispersant approval (Environment Canada 1984). The results showed that Brand S has an LC₅₀ greater than 1,000 mg/l and would be acceptable for use under Canadian guidelines.

TABLE 6
EFFECTIVENESS OF COREXIT 9527 AND BRAND "S" COMBINED
(Percent Dispersed)

TEMPERATURE (DEG C)	Dispersant Only	Dispersant and Brand "S"
0	73 69	70
5	75 71	88
10	80 76	91 80 (I/O=1:4000)
15	98	--

Notes: Dispersant was applied to the oil surface in droplet form from an Eppendorf pipette.

Dispersant to oil ratio was 1:20.

Oil and inhibitor were premixed together and then discharged onto the water surface.

I/O is the inhibitor to oil ratio which, unless is otherwise stated, was 1:500.

TABLE 7
EFFECTIVENESS OF COREXIT 9550 AND BRAND "S" COMBINED
(Percent Dispersed)

TEMPERATURE (DEG C)	Dispersant only (Dispersant to Oil)	Dispersant and Brand "S"
0	69 (1:20)	83
5	91 (1:20)	--
	76 (1:50)	81
	36 (1:100)	37
10	96 (1:20)	--
15	88 (1:100)	93

Notes: Dispersant was applied to the oil surface in droplet form from an Eppendorf pipette.

Dispersant to oil ratios appear in brackets.

Oil and inhibitor were premixed together and then discharged onto the water surface.

MESO-SCALE EFFECTIVENESS TESTS

Purpose

The goal of this series of tests was to evaluate the effectiveness of the emulsion inhibitor in a larger system over longer periods of time, and in a more realistic energy environment characteristic of lower sea states.

Methods

The tests were conducted in a wind/wave tank (Plate 2) 11 m long, 1.1 m wide and 1.55 m high. Ten thousand litres of fresh water (a depth of 0.85 m) and two litres of oil were used in each test. Fresh water rather than salt water was used for these runs to simplify test preparations. Figures 20 and 21 show that water salinity had no effect on inhibitor performance in the hoop tank.

The test matrix was as follows:

- * two crude oils (Avalon J-34 and Alberta Sweet Mixed Blend)
- * four inhibitor-to-oil dose rates (0:1, 1:10,000, 1:5000 and 1:1000)
- * two temperatures (about 10°C and 15°C)
- * two combinations of wind and wave height (1m/s and 17 cm (energy level 1) vs 2m/s and 20 cm (energy level 2)).

The wind opposed the direction of wave travel in order to hold the slick in the centre of the tank. Wind profiles, wave studies and dye/mixing studies can be found in the report.

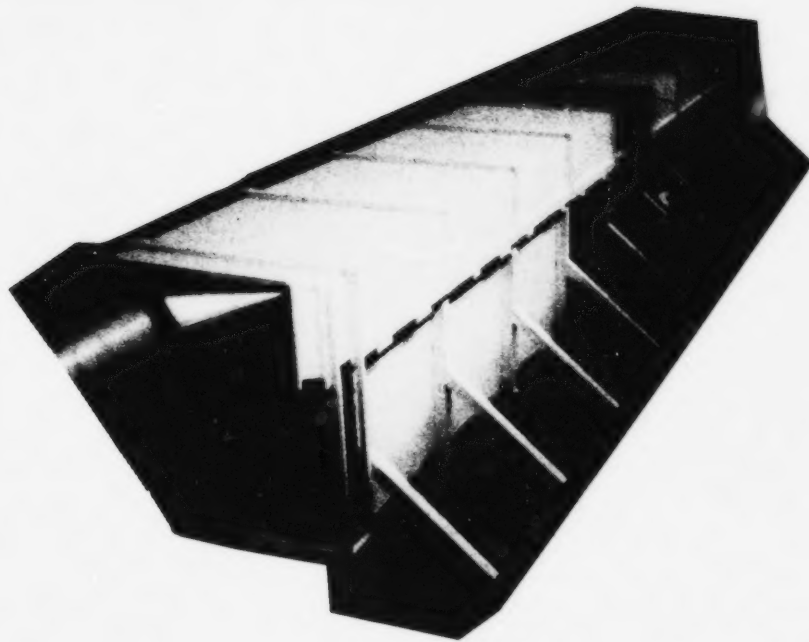


PLATE 2 - WIND/WAVE TANK

The test procedure was as follows:

- 1 fill the tank with 10,000 L of fresh water; adjust temperature to 10° or 15°C by adding hot water
- 2 set the fan and wave generator to achieve either energy level 1 (1m/s wind, wave generator stoke of 25 cm at 0.9 Hz) or energy level 2 (2m/s wind, wave generator stoke of 25 cm at 1 Hz)
- 3 gently pour 2 L of the test oil premixed with the inhibitor diluted 1:10 in toluene onto the water at the centre of the tank
- 4 take water column samples (100 ml) (from top, middle and bottom parts) and slick samples (using a plexiglass slide to adsorb emulsion) at 15, 30, 45, 60, 90 and 180 minute intervals (some tests were run as long as 24 hours)
- 5 analyse the oil content of water and water content of oil (as specified for the hoop tank tests)
- 6 after each run, turn off wave generator, allow oil to resurface and wipe and skim up any surface oil

The tank was not refilled for each run because of the time involved in heating tap water from 20°C to the desired temperature. The tests were configured in groups by temperature, energy level and surfactant concentration. For a given temperature and energy level the tank was cleaned and the different concentrations tested in increasing order (i.e., undosed oil first, 1:10,000 second, 1:5000 third and 1:1000 last) so that any inhibitor remaining after removing the oil would not interfere with the next, higher dosage test.

Results and Discussion

Table 8 gives a summary of the conditions and results of the tests.

Figure 26 shows the effect of inhibitor dosage on the water uptake of J-34 oil at 15°C and energy level 1. With no inhibitor present the oil rapidly takes up water to form balls of emulsion about 5 cm in diameter, surrounded by a thin sheen of oil. The oil samples were taken from these balls. Oil that drifted to the end of the tank was heavily emulsified into a brown mousse by the action of breaking waves. Though dispersion samples were taken for all runs, only in two cases of twenty three were dispersed oil concentrations above the lower limit of detectability of 10 ppm. As such, no reliable data on the enhancement of dispersion are available for most of the runs.

As the surfactant dose increases emulsification is inhibited more effectively. At 1:10,000 the water content is reduced to about 50% and the emulsion is in the form of balls about 2.5 cm in diameter with about 250 to 300 balls per square metre on the water surface.

At a 1:5000 dose of inhibitor the water content is reduced to about 40%. The oil took the form of 2 cm diameter balls with about 300 to 400 per square metre. No dispersion was evident or detected. At 1:1000 most of the oil remained as a coherent slick about 2-3 mm thick with a water content of only 30%. Dispersed oil concentrations were measured at approximately 20 to 30 ppm, a noticeable increase over the previous runs.

Figure 27 shows the same tests conducted at 10°C. The appearance of the undosed slick was identical to that at 15°C and both achieved the same water content (70%). The effectiveness of the surfactant at 1:10,000 appears better at 10°C than at 15, though with a margin of error in water contents of 8% this may not be a real difference. Certainly the performance of the surfactant at doses 1:5000 and 1:1000 at 10°C is indistinguishable from that at 15°C. It seems that at the lower energy levels represented by these tests the effects of declining temperature are not as pronounced as in the previous tests. For example, in the shaker tests (Ross et al 1985) at 20°C,

TABLE 8

SUMMARY OF WIND/WAVE TANK TRIALS

RUN	WATER TEMP (°C)	ENERGY LEVEL	OIL TYPE	SURFACTANT TYPE	SURFACTANT: OIL CONCENTRATION	FINAL EMULSION WATER CONTENT (%)
1	15	2	J-34		0:1	65
2	15	1	J-34		0:1	70
3	15	1	J-34	Brand S	1:10,000	50
4	15	2	J-34	Brand S	1:10,000	45
5	15	1	J-34	Brand S	1:5000	40
6	15	2	J-34	Brand S	1:5000	36
7	15	2	J-34	Brand S	1:1000	30
8	15	1	J-34	Brand S	1:1000	35
9	10	1	J-34		0:1	73
9A	10	2	J-34		0:1	70
10	10	1	J-34	Brand S	1:10,000	45
11	10	2	J-34	Brand S	1:10,000	45
12	10	1	J-34	Brand S	1:5000	40
13	10	2	J-34	Brand S	1:5000	40
14	10	1	J-34	Brand S	1:1000	37
15	10	2	J-34	Brand S	1:1000	35
16	10	1	ASMB		0:1	68
17	15	1	ASMB		0:1	65
18*	15	1	ASMB	Brand S	1:1000	62
23*	15	1	J-34	Brand S	1:1000	50

J-34 East Coast Oil

MSW Mixed Sweet Western Oil

* 24 hour run

FIGURE 26 EMULSIFICATION VS TIME (J-34)

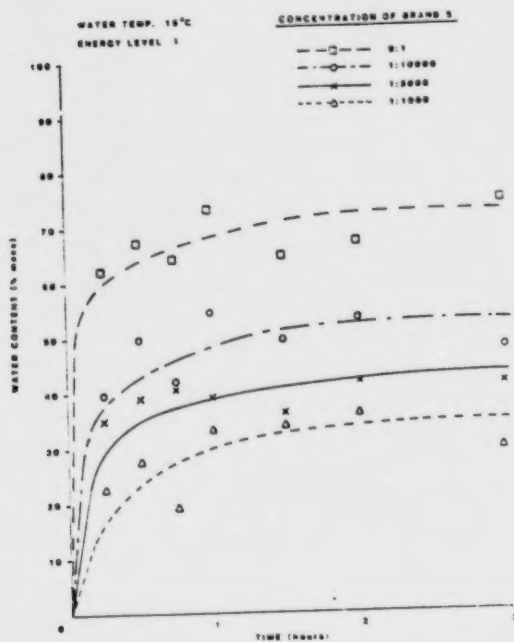


FIGURE 27 EMULSIFICATION VS TIME (J-34)

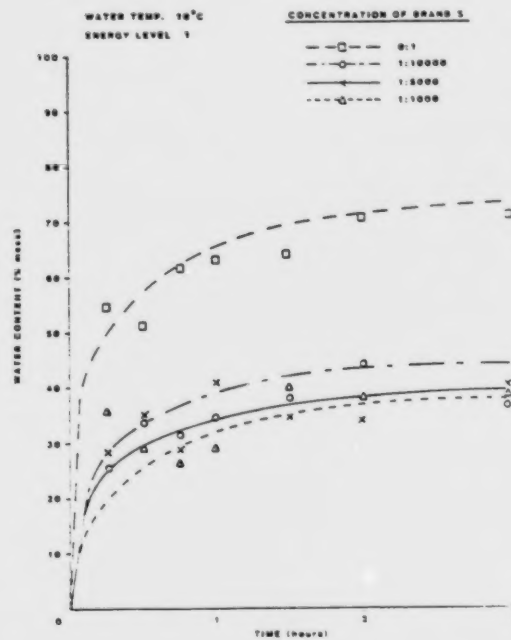


FIGURE 28 EMULSIFICATION VS TIME (J-34)

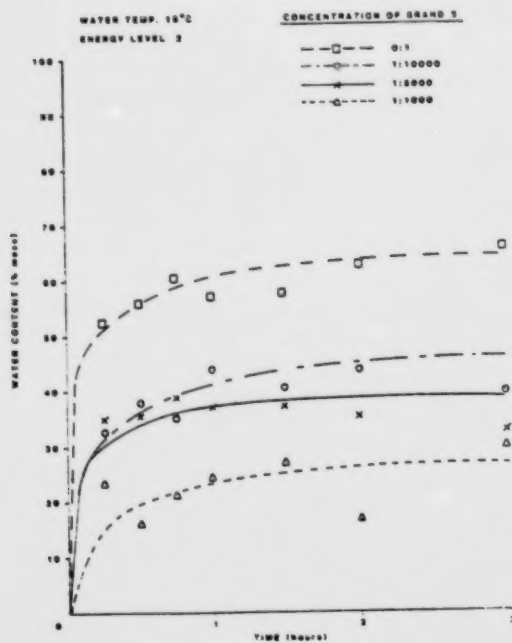
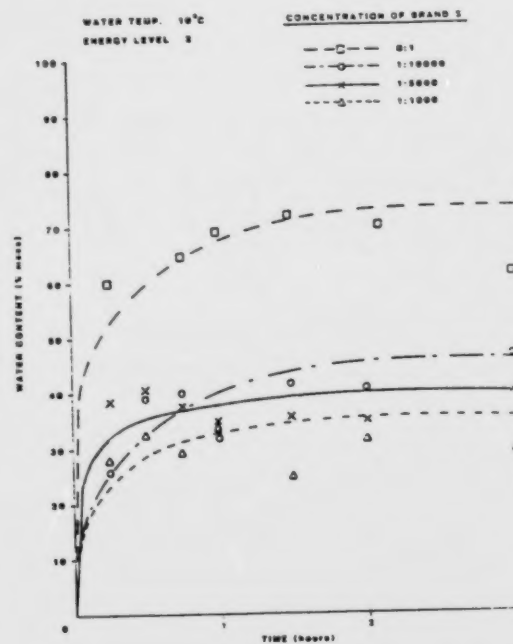


FIGURE 29 EMULSIFICATION VS TIME (J-34)



Brand S is effective on fresh J-34 oil at 1:20,000 at 20°C but not at 10°C. The concentration has to be increased to 1:5000 to be effective at the lower temperature. In the hoop tank tests Brand S is marginally effective on fresh J-34 oil at 1:10,000 at 20°C; the concentrations must be increased to 1:5000 at 10°C to be effective. At these concentrations the oil totally disperses. In the wind-wave tank at 15°C and 10°C there is little difference between dosages of 1:10,000, 1:5000 and 1:1000.

At constant temperature, as the energy level increases the inhibitor becomes more effective; the increased mixing probably simply enhances the rate of collision and coalescence of water drops in the oil. At constant mixing speed, inhibitor effectiveness declines with declining temperature, probably because the increased oil viscosity reduces both the collision rate and settling rate of water drops. Reducing temperature (as long as the oil does not cool too much and gel) does not seem to affect final water content though it does appear to increase emulsion stability through hindered settling of water droplets.

Under conditions of low temperatures and low mixing levels, such as the levels available in the wind/wave tank, where emulsification of the chemical-free oil is itself inhibited due to viscous oil and a lack of sufficient energy to produce a mousse containing small water drops, a small amount of inhibitor becomes effective in preventing significant water incorporation. Increasing the concentration only slightly improves the situation.

Figures 28 and 29 provide similar results for the tests done at energy level 2 (2 m/s wind against 20 cm waves): very little difference in inhibitor effectiveness at the two temperatures and only a slight increase in effectiveness over an order of magnitude in concentration (1:10,000 reduces the water content from 70 to about 40%, 1:1000 reduces it to about 25%). Comparison of Figure 28 with Figure 26 and Figure 29 with Figure 27 indicates that the inhibitor is generally more effective at the higher energy level; this is consistent with the results in the hoop tank.

Figure 30 shows the effect of inhibitor addition on the emulsification of Alberta Sweet Mixed Blend (ASMB) crude oil. At 10°C the oil forms an emulsion in about one hour, at 15°C it takes two to three hours. This, again, illustrates the dependence of emulsification rate on temperature; as the oil becomes more viscous (above the temperature at which it gels) emulsification proceeds faster.

At an inhibitor dose of 1:1000 the oil almost completely dispersed over a period of two hours (Figure 31). Dispersed oil concentrations reached about 250 ppm for 1.5 hours. A concentration of 200 ppm represents complete dispersion throughout the entire tank. There was very little of the original 2 L of oil left on the surface after 2 hours, barely enough to sample. However, after 4 hours much of the dispersed oil had resurfaced and coalesced to form a slick with a water content of about 50%. One explanation for this is that leaching of the inhibitor into the water phase occurred because of the much greater interfacial area for mass transfer created by the dispersion process itself.

Figure 32 shows the results of 24-hour tests with the ASMB and J-34 oils. For the ASMB case the oil virtually completely dispersed with peak concentrations of 250 ppm (see Figure 31). The oil, after 24 hours, though weathered, still had not formed a "mousse". For the J-34 case, virtually no dispersion of the dosed slick took place and the inhibitor retains its effectiveness for the entire test. The final water content was about 50% and the oil was in the form of droplets about 25 mm in diameter. In the undosed case the oil had formed a thick, 75% water emulsion. It seems that, if the inhibitor does not greatly enhance dispersion (as it does with the ASMB oil), it stays with the oil for long periods, preventing the formation of stable emulsions.

FIGURE 30: EMULSIFICATION VS TIME (ASMB)

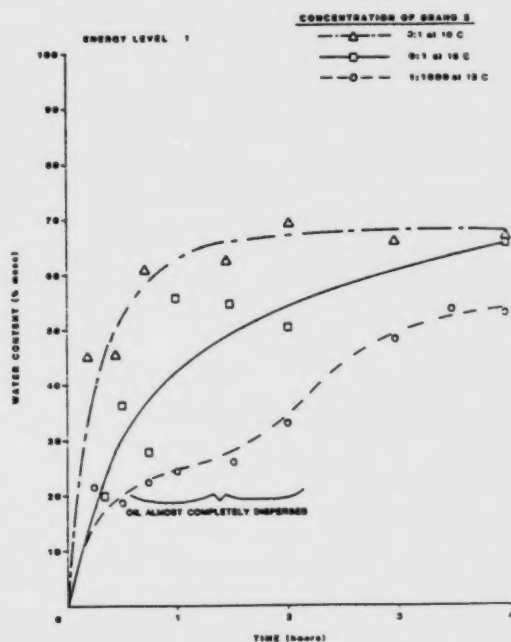


FIGURE 31: DISPERSION VS TIME (ASMB)

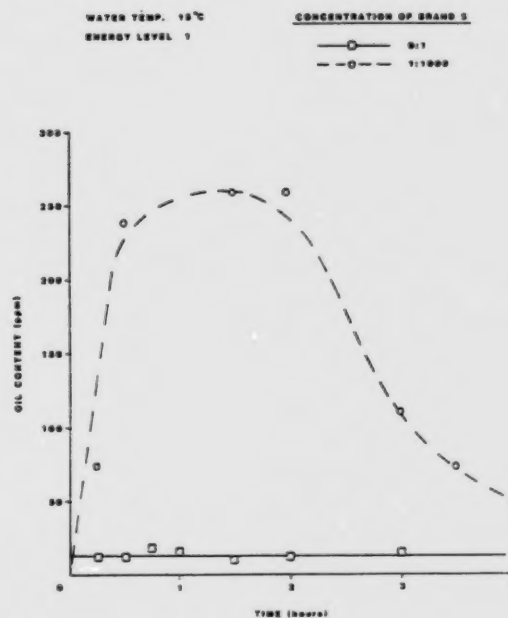
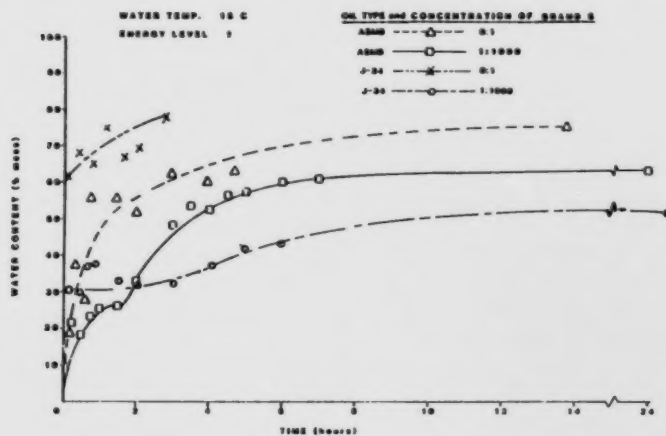


FIGURE 32: EMULSIFICATION VS TIME



MODELLING

A mathematical model describing the processes of emulsification and dispersion, the competition between the two and the effect of inhibitor addition on the rates of the two processes is being developed. The model has been constructed but had not been fully tested at the time of writing. Basically, it combines the emulsification equations proposed by Mackay and Zagorski (1982) with the natural dispersion equations of Buist (1979) and S.L. Ross (1984) in a unified finite difference model suitable for computerization.

SUMMARY AND CONCLUSIONS

The surfactant, Brand S, has been shown to be an effective emulsion inhibitor at very low concentrations. Two factors seem to be the prime determinants of its performance, oil viscosity and surfactant concentration. As an oil weathers and/or cools more surfactant is required to maintain the oil in an unemulsified state. It seems likely that this is due to the increased viscosity of the continuous oil phase, since viscosity is the only property that changes dramatically over the ranges of temperature and weathering investigated. It is unclear what specifically reduces the effectiveness of the surfactant as viscosity of the oil increases; it is probably a combination of reduced mobility of the chemical in the oil, reduced drainage rates of oil between closely approaching water droplets and lower settling rates of water droplets. The precipitation of waxes or other interface stabilizing compounds in the oil at oil-water interfaces, as temperatures decrease, may also be a contributing factor.

It is interesting to note that the above analysis does not hold for situations where the ambient temperature is much less than the pour point of the oil. Results show that when the temperature is about 20°C below the pour point, the oil no longer emulsifies but rather becomes highly viscous and takes the form of non-coalescing, semi-solid, smooth, spherical particles.

One unexpected benefit of adding the emulsion inhibiting chemical to the oil is that it greatly enhances dispersion rates, even at very low concentrations. Complete dispersion of the oil in the hoop tank was noted for concentrations as low as 1 part Brand S in 5000 parts oil. At these concentrations, a conventional dispersant produced little enhancement.

Four regimes of emulsion prevention can be identified with respect to inhibitor concentration. First, with no inhibitor present the oil rapidly forms a stable, highly viscous, brown emulsion. Second, at certain low concentrations of inhibitor the oil still emulsifies into a black coloured product but the entrained water droplets are larger and the water content, viscosity and stability of the emulsion are lower than the emulsion formed with the inhibitor-free oil. Third, at higher inhibitor concentrations, emulsion formation is prevented and the oil remains on the surface as a black, relatively non-viscous layer. At this stage, dispersed oil concentrations are about two or three times higher than the case for untreated oil. Finally, at still higher inhibitor concentrations the slick is completely dispersed into the water phase.

The effectiveness of the surfactant is also related to mixing energy: the higher the mixing energy the more efficient is the chemical. With no surfactant present, higher mixing energies result in more quickly formed and more stable emulsions. At borderline surfactant concentrations higher mixing energies result in a greater delay in the emulsification process, but no effect on the final equilibrium water content is apparent. At higher concentrations no effect of mixing energy is apparent although dispersed oil concentrations are elevated at higher mixing levels.

In summary, it is apparent that the surfactant, Brand S, has two effects on emulsifiable oils. The first is a reduction in oil-water interfacial tension which promotes the dispersion of oil droplets in water, and the second is some (as yet unknown) effect on the water droplets or the stabilizing film surrounding them which greatly enhances recoalescence of the entrained drops. This latter effect inhibits or prevents emulsion formation. For actual oil spills at sea it is easy to surmise that both effects working in tandem would promote the complete dispersion of the oil over time.

The results of dispersant effectiveness tests show that Brand S in low concentrations dramatically enhances dispersion rates at temperatures above 10°C. Results are less dramatic at temperatures below 10°C. In addition, when used in conjunction with conventional dispersants, Brand S seems to enhance the effectiveness of the dispersants, but only slightly. As might be expected, the effectiveness of Brand S improves as its concentration increases and also when the product is premixed into the oil rather than added dropwise during the experiment.

The meso-scale testing showed that Brand S effectively inhibits emulsification in simulated low sea state conditions as well as at high mixing energies. At the lower energy levels (17 to 20 cm waves, 1 to 2 m/s winds) the effects of declining temperature are not as pronounced as in the smaller-scale tests and the effects of increased inhibitor dose are not as dramatic.

When the inhibitor was added to the ASMB oil the oil completely dispersed, although the chemical may have thereafter leached out of the oil over a two or three hour period. When the inhibitor was added to the J-34 oil, rapid dispersion did not occur but the chemical remained with the oil to prevent the process of emulsification. In either case the effect is advantageous in terms of dealing with oil spills at sea. In the former case the oil will rapidly disperse at sea and will not likely resurface to form an emulsifiable slick; in the latter case, rapid dispersion will not occur but gradual dispersion will be allowed to proceed because the surface oil's tendency to form a viscous emulsion will have been curtailed.

ACKNOWLEDGEMENTS

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COMBUSTION OF OIL ON WATER

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ABSTRACT

This report contains the results of measurements performed on both 0.4 m and 0.6 m diameter pool fires produced by burning a layer of Prudhoe Bay crude oil supported by a thermally deep layer of water. Both steady and vigorous burning caused by boiling of the water sublayer were observed. The measured energy release rate for steady burning was about 640 kW/m^2 . The emission rate, the size distribution, and specific extinction coefficient were measured for the smoke aerosol produced by the fires. Data were also obtained on the structure of the smoke aerosol by electron microscopy and on emission of CO and CO₂. Analysis of the crude oil burn residue indicated selected depletion of the short chain alkanes and cycloalkanes when compared to the fresh oil. Mono-ring aromatics including benzene, toluene, and xylenes present in the fresh crude were absent in the burn residue. Calculations of the induced air flow into a simulated distribution of 20 fires over a $100 \text{ m} \times 100 \text{ m}$ area showed that the maximum inflow velocity near the largest size fire (2.5 m diameter, 3.2 MW) was 1.1 m/s.

BACKGROUND

In 1985, the Center for Fire Research (CFR) at the U.S. National Bureau of Standards (NBS) began studies of oil spill combustion under support from the U.S. Minerals Management Service (MMS). This work seeks to understand the process of oil spill combustion on open waters and in water filled channels formed in broken ice. This work is intended to be a cooperative effort leading to results that may be used to generalize specific measurement of oil spill burn efficiency performed by Smith and Diaz at the EPA-OHMSETT facility in Leonardo, NJ [1]. The scope of the original work has been broadened by added support from Environment Canada and the U.S. Coast Guard to include calculations and measurements related to induced air flow velocities in the area of the fire, burn residue chemical composition, and smoke production from the oil spill burn.

The long range goal of the research program is to provide a means to make quantitative predictions of the fraction of oil in a spill that can be consumed by an in-situ combustion process, the characteristics of the residual oil, and the characteristics of the combustion product flow from the burn. It is hoped that this information may be cast into a form that is readily useable by local officials and oil spill response professionals as part of their decision making process in the event of an oil spill.

As a first step in this research program a framework for detailed study and calculation of the open water oil spill combustion process was formulated by Wichman [2]. It was clear from this initial work that to obtain an overall understanding of oil spill combustion and to produce sound technical quantification of the important effects of combustion, such as the beneficial consumption of oil and detrimental smoke production, closely coordinated experimental and theoretical studies must be conducted. To address many

aspects of the oil spill combustion process, both for confined and unconfined spills, an interdisciplinary research team was assembled within the Center for Fire Research at the U.S. National Bureau of Standards. This team brings together expertise in combustion, fire dynamics, computational fluid flow, particulate measurement, and chemical analysis. All members of the team are contributors to this paper which contains quantitative results for confined oil spill energy release rate, thermal radiation, smoke production, induced air flow, and chemical composition changes between the fresh oil and burn residue.

EXPERIMENTAL FACILITY

Test work in this study was conducted in the CFR large scale testing facility in which a calorimeter hood was used. The experimental facility accommodates oil pool fires up to 0.6 m in diameter. This facility is used cooperatively with studies funded by U.S. Defense Nuclear Agency. A schematic drawing of the instrumented hood is shown in Figure 1. Liquid pool fires are situated under the 2.4 m x 2.4 m collection hood with an adjustable exhaust rate up to about 2 m³/s (4000 ft³/min). A tripper plate at the stack inlet insures uniform mixing of combustion products and dilution air before the gases are sampled five duct diameters downstream of the inlet. The mass loss of the burning fuel floated on a deep water layer is monitored using a water cooled load cell with a sensitivity of about 3 grams. Thermal radiation from the fire is measured with a Gardon-type radiometer located several pool diameters from the pan.

Energy release rate from the fire is determined using oxygen consumption calorimetry. This method is based on the fact that the heat of the combustion is about 13 kJ/g of oxygen consumed for all hydrocarbon fuels [3,4]. Thus measurements of O₂ concentration and total flow rate through the stack made downstream of the horseshoe section in the duct are used to calculate the O₂ consumption rate and proportional energy release rate of the fire.

Other measurements in the exhaust duct relate directly to measurement of smoke production and soot particulates. A cascade impactor with seven stages and a backup filter was used for monitoring the aerodynamic size distribution of the aerosol. Quartz fiber filters were used as the collection substrate to minimize the smoke particle bounce that might occur on a flat metal substrate. Particle bounce could be significant for the solid, agglomerate type particles making up the smoke aerosol. Each collection substrate including metal disk and filter were weighed to the nearest 0.01 mg. The sampling flow was about 22 l/min and a conical probe with 0.64 cm orifice was used to insure isokinetic sampling at a velocity of about 10 m/s. The impactor was preheated in a convection oven for thirty minutes and then was rapidly positioned in the stack just before igniting the crude oil pool. This was done to minimize moisture condensation on the impactor stages.

The filter collection system, illustrated in Figure 2, allowed for the sequential collection of three filter samples over the course of a pool fire test. The transfer line, manifold, and filter holders were all heated to match the stack temperature during the burn. This was done to minimize the evaporation/condensation of the smoke aerosol during transport or on the filter and to minimize the thermophoretic driven deposition of particles on the walls. The sample flow, about 10 l/min, and nozzle inlet, 0.48 (3/16 inch), were selected to insure isokinetic sampling. The all glass construction of the filter collection system allowed ready inspection of deposition

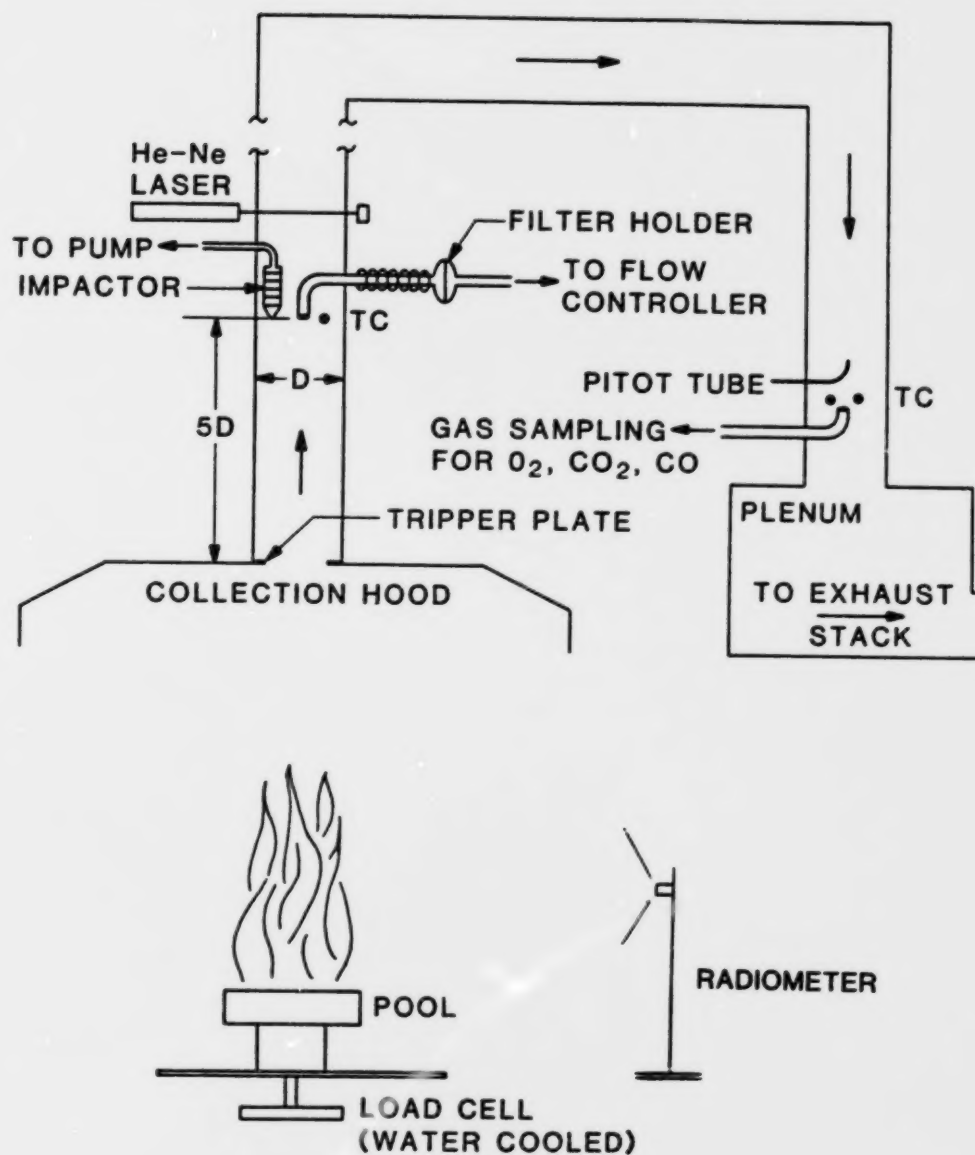


FIGURE 1. INSTRUMENT HOOD FOR OIL BURN EXPERIMENTS

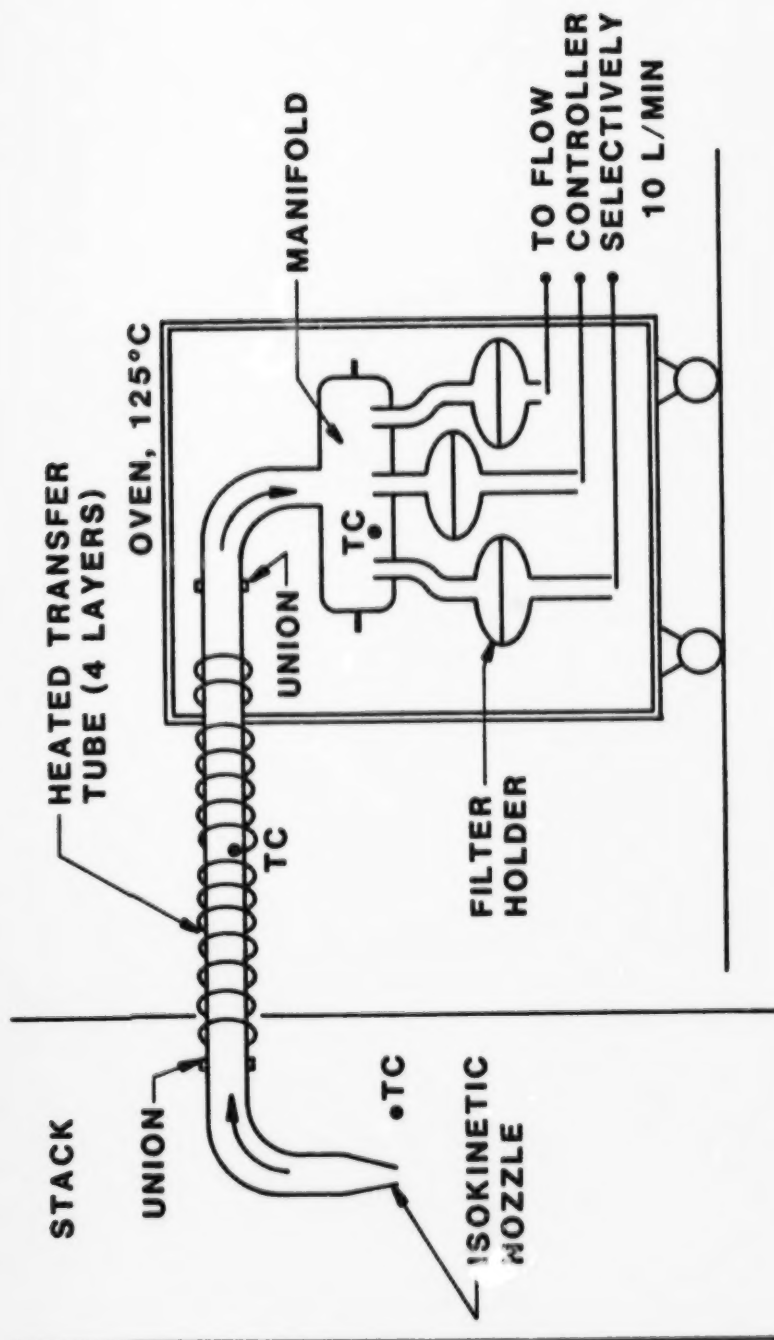


FIGURE 2. 3-FILTER, ALL GLASS, SMOKE COLLECTION SYSTEM

and ease in cleaning. The transmittance of a He-Ne laser, $\lambda = 633 \text{ nm}$, through the smoke in the stack, 0.48 m pathlength, was monitored with a photometer and ratioed to the incident laser intensity to compensate for variations in the source intensity. The design of the photometer is reported by Babrauskas [5]. The laser beam is located about 1 m above the sampling probes. The optics are purged with room air to avoid smoke deposition on the lenses during a test. The uncorrected optical densities (OD's) derived from the transmittance measurements agreed to within 5% with the values of neutral density filters. The OD's of the smoke aerosols were in the range 0.3-1.5. The transmittance measurement is essentially instantaneous and thus provides an indication of the fluctuation in the smoke concentration in the stack.

The gas sampling probe, pitot tube, and thermocouples are located downstream of the horseshoe section of duct. The gas velocity in the stack was determined from the pitot tube measurement together with the thermocouple reading. The sampled gas was cooled with a dry ice trap to remove water vapor, filtered, and then drawn into the gas analyzers. Non-dispersive infrared detectors are used for monitoring the concentrations of CO and CO₂. This information is used in determining the smoke emission based on the carbon balance method.

Samples for study using a transmission electron microscope (TEM) were obtained by rapidly inserting a carbon coated TEM grid into the stack for a few seconds. The primary collection mechanism under these conditions is thought to be via thermophoresis.

CRUDE OIL SAMPLES

Three different crude oils were obtained for study from supplies at EPA-OHMSETT. These were Murban, Larosa, and Prudhoe Bay North Shore crude oils. Testing performed in this study has been limited to evaluations of the Prudhoe Bay North Shore crude oil.

Samples of Prudhoe Bay North Shore crude oil were burned in both 0.4 m and 0.6 m diameter pans. In both cases the oil was floated on a thermally deep layer of water. Emphasis is given in this report to analysis of the combustion process measured in tests with the larger 0.6 m diameter pool fires. Partial results from each of two 0.4 m and two 0.6 m diameter pool fires are given.

ENERGY RELEASE RATE

Figure 3 shows the history of the energy release rate from one of the 0.6 m diameter pool fires. The energy release rate of the burning oil rises rapidly after ignition and flame spread across the surface to a plateau value of about 180 kw (640 kW/m²). As seen in Figure 3, the energy release rate remains steady through most of the test, but increases dramatically during the last 30 seconds of the burn when the amount of oil left on the water surface is small. The burning rate during this vigorous combustion increases by more than a factor of two. Radiation levels increase to such an extent that the positions where once it was tolerable to stand and observe the experiment now become too close for human comfort. The sublayer of water under the oil can be seen to be boiling vigorously. This boiling persists even after the flames extinguish. The two burning regimes can be seen in Figure 4, photographs of a 0.4 m diameter pool fire experiment. Energy release rates and thermal radiation from both the 0.4 m and 0.6 m diameter pool fires are quantified in

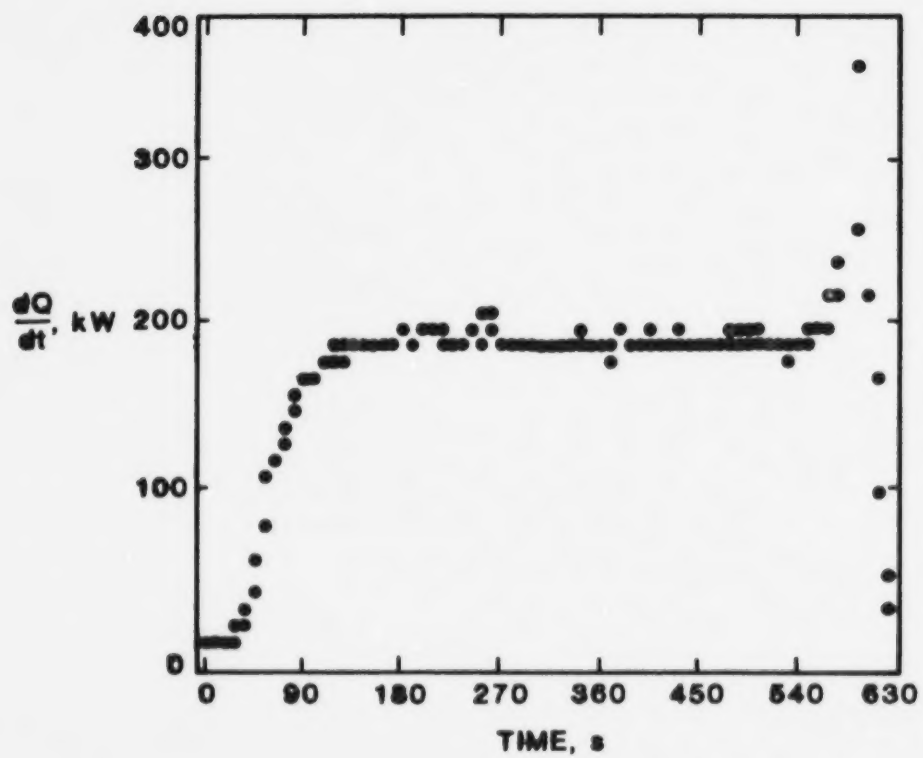


FIGURE 3. RATE OF ENERGY RELEASE FOR PRUDHOE BAY CRUDE OIL BURNED IN A 0.4 METER DIAMETER POOL.

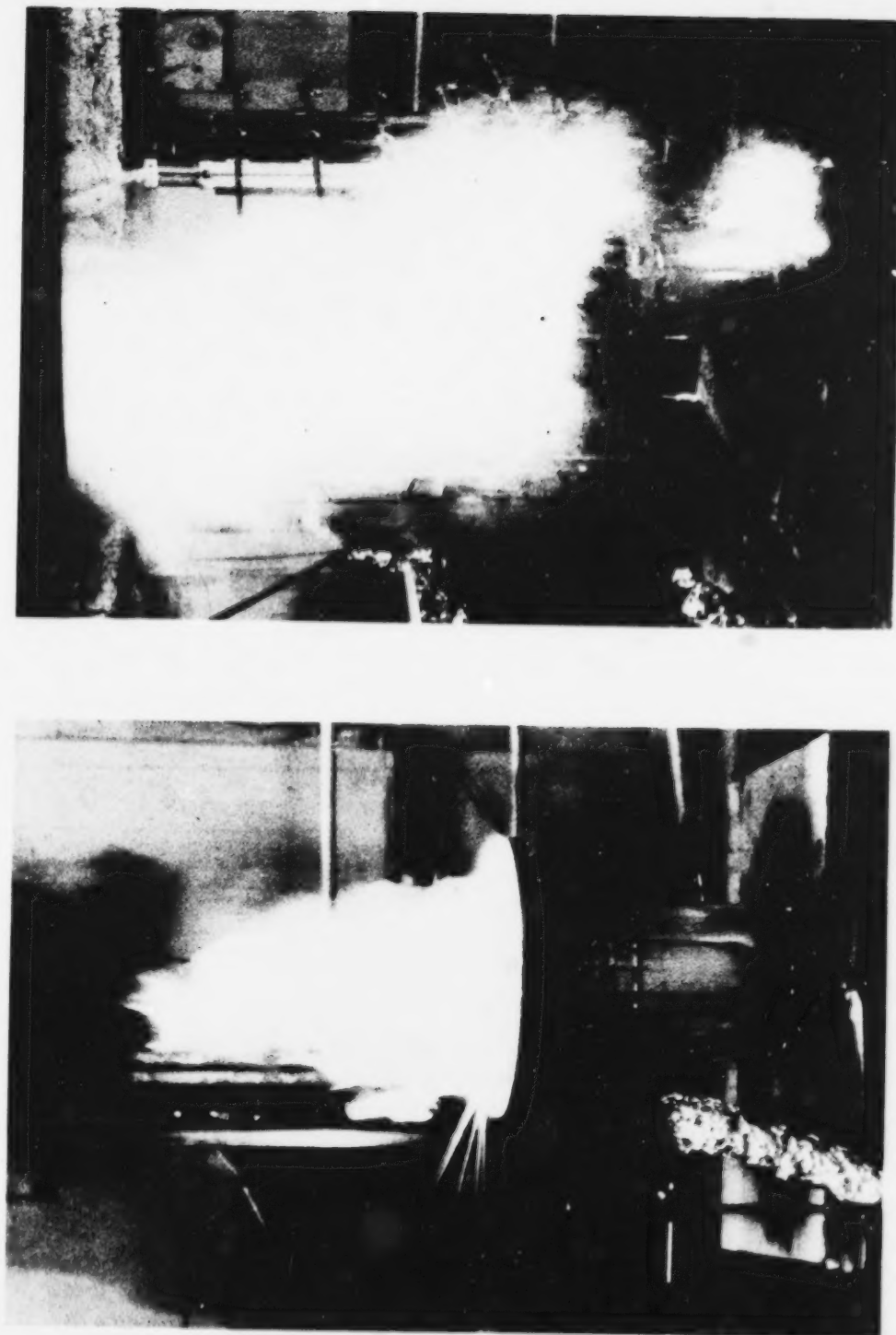


FIGURE 4. PRUDHOE BAY CRUDE OIL FIRE IN 0.4 METER DIAMETER PAN
(LEFT) STEADY BURNING
(RIGHT) VIGOROUS BURNING AT THE END OF THE TEST

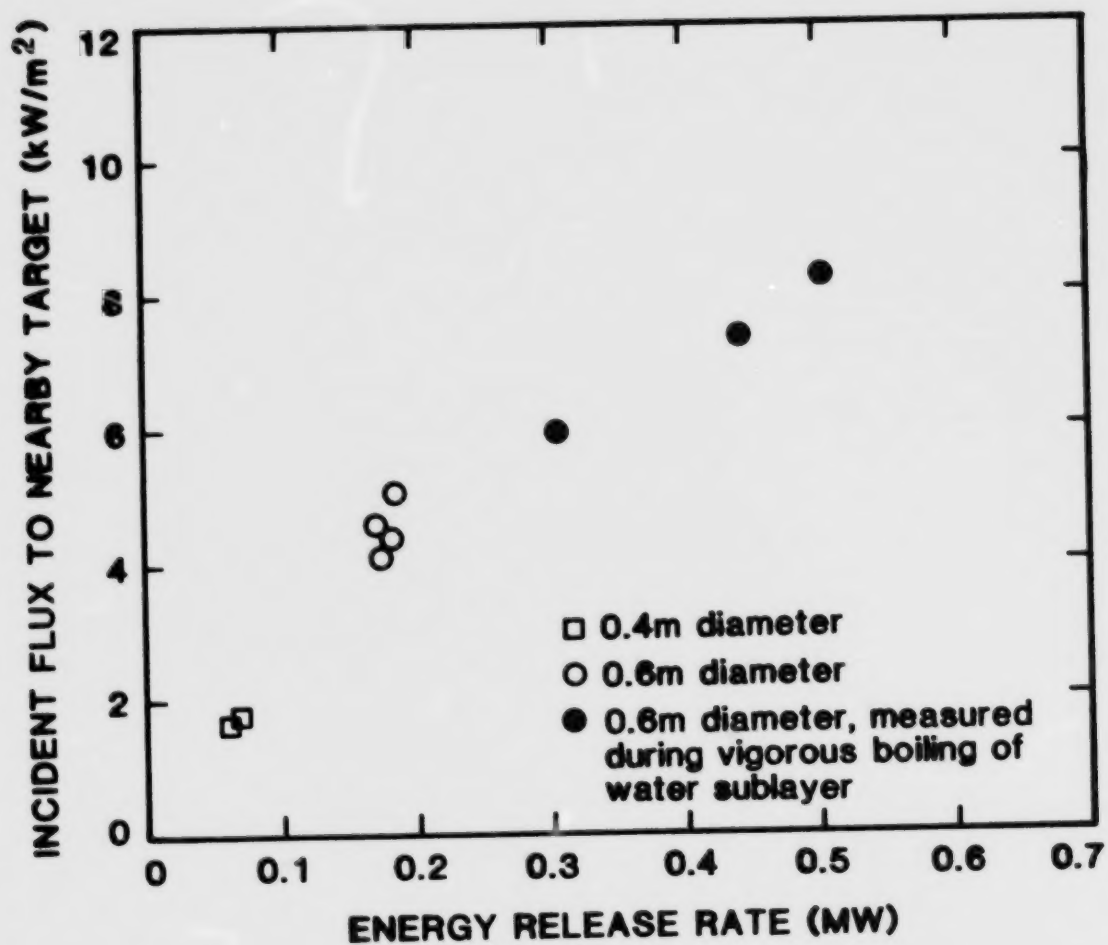


FIGURE 5. RADIATION AND ENERGY RELEASE RATE FROM PRUDHOE BAY CRUDE OIL POOL FIRES.

Figure 5 for both the steady burning period (open symbols) and the vigorous but short burning period before flame extinction (filled symbols). The largest energy release rate measured for the 0.6 m diameter pan was 0.5 MW (1800 kW/m^2) during the vigorous burning period. This vigorous burning period appears as the oil layer becomes thin and sufficient energy from the hot surface and flame causes the supporting water layer to boil. The erupting surface lifts droplets of oil into the flame accelerating the burning process and increasing the energy feedback to the water sublayer which enhances the boiling. Quantification of this process will be part of studies underway involving temperature measurements with rakes of thermocouples immersed in the oil and water layer during burning. The partitioning of energy and its relation to film thickness are important characteristics of the oil combustion process that need to be understood.

SMOKE MEASUREMENT

The smoke aerosol sampling techniques used in this study are suitable to quantify smoke production only during the nominally steady state burning of the oil and not during the relatively short transient period at the end of the burn when vigorous boiling of the water sublayer increases the combustion rate.

Qualitatively there are indications that the smoke aerosol produced during this intense burning contained a tarry component soluble in toluene, in addition to the low density, sooty particles produced during the steady state combustion. A tarry residue was observed on both the impactor and filter nozzles which extend into the exhaust duct. Apparently this resulted from tarry droplets generated during the intense burning impacting on the nozzles. In one experiment, a tarry residue was observed within the impactor, and this was the one experiment in which smoke from the intense burning at the end of the fire was collected. Further discussion of smoke production will be limited to analysis of the steady burning period.

Light Extinction

The light extinction K is related to the light transmittance, I/I_0 , via Bouguer's law,

$$I/I_0 = e^{-KL}, \quad (1)$$

where L is the path length in meters. As seen in Figure 6, the value of K has a large variability around a fairly constant mean value of about 2 m^{-1} . This large variability is a result of the pulsating characteristic of buoyant plumes in which puffs of smoke can be seen arising from the flame at a frequency of a few Hz. The other instruments, including the gas analyzers and thermocouples, have response times of several seconds and thus do not pick up this pulsation.

In addition to the extinction coefficient, there are two reduced extinction coefficients of interest. The first is K_s , the extinction coefficient per mass concentration of smoke, m_s

$$K_s = K/m_s \quad (2)$$

The quantity K_s is an intrinsic property of the smoke depending on the wavelength of light, the optical properties of the smoke, and the size distribu-

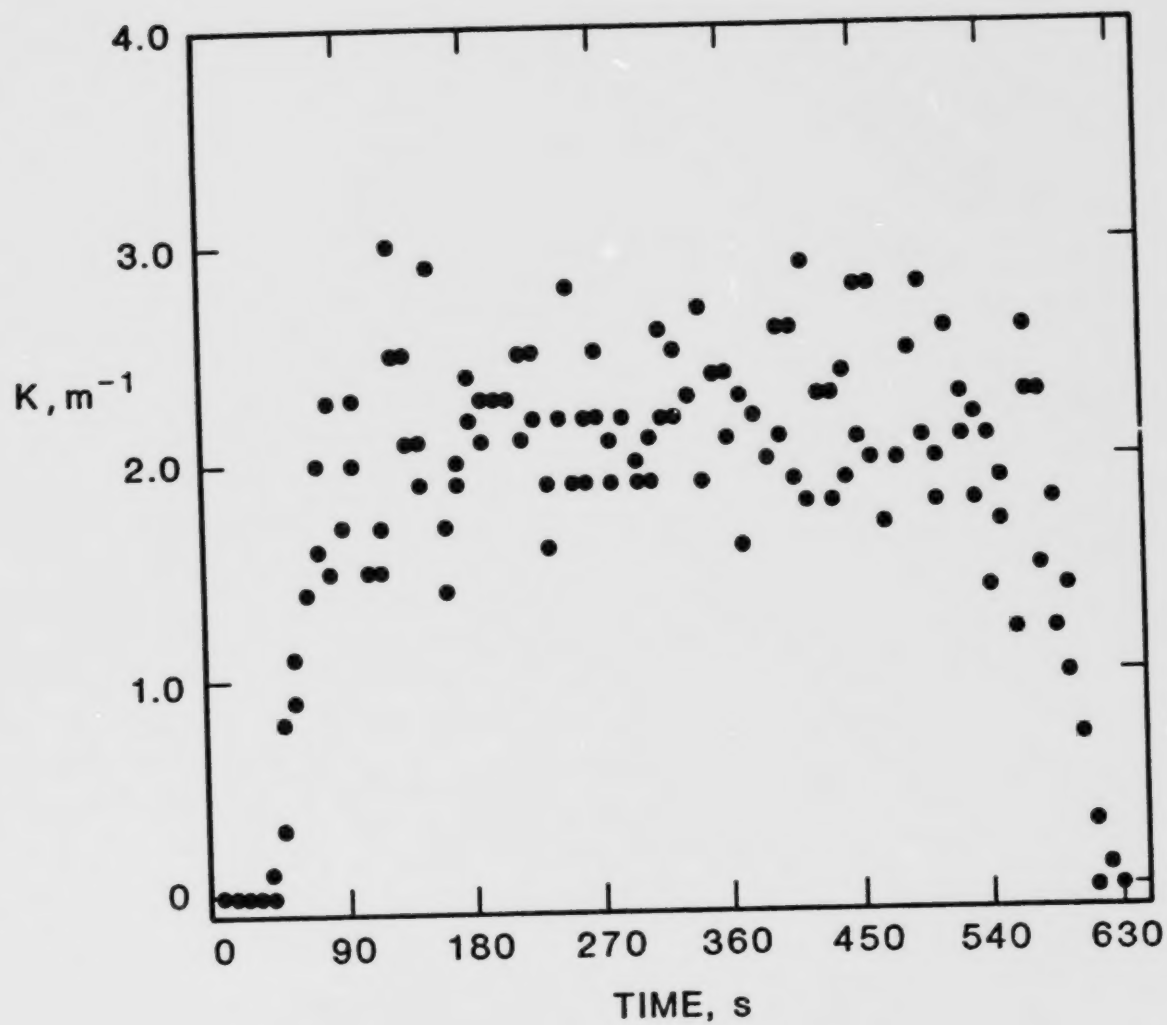


FIGURE 6. LIGHT EXTINCTION COEFFICIENT FOR PRUDHOE BAY CRUDE
BURNED IN 0.6 METER DIAMETER POOL.

tion of smoke. As indicated in Table 1, K_g is relatively constant during the burn and has a mean value of $8.8 \text{ m}^2/\text{g}$. This is to be compared to Seader and Einhorn's [6] value of $7.6 \text{ m}^2/\text{g}$ obtained from smoke produced during the flaming combustion for a variety of fuels including wood and plastics. Some difference in the results is expected since Seader uses a white light source while a monochromatic source with $\lambda = 633 \text{ nm}$ is used in this study.

The second reduced extinction coefficient, K_f , is the extinction coefficient per unit mass loss concentration,

$$K_f = K/(dm/dt/dv/dt) \quad (3)$$

where dm/dt is the sample mass loss and dv/dt is the volumetric flow rate of gas up the stack. One advantage of this quantity is that a measurement of the smoke concentration is not required. The plot of K_f in Figure 7 suggests that there is a gradual increase in K_f with respect to time. This trend may result from the higher vapor pressure paraffin component of the fuel burning preferentially early in the test with a lower soot yield while the higher sooting aromatic and asphaltene components burn at the later stage.

Smoke Emission

Two methods were used for determining the smoke conversion factor ϵ , which is defined by

$$\epsilon = \text{mass of smoke aerosol produced/mass of fuel burned}$$

The first method, termed the flux method, is based on the measurement of the smoke collected on the filter, m_s , and on the mass loss of the sample, m_L , over the same time period. The factor ϕ , which equals the ratio of the mass flow of air up the stack to the mass flow to the filter, accounts for the small fraction of the total smoke yield sampled.

$$\epsilon_1 = (m_s/m_L)\phi \quad (4)$$

The second method is the carbon balance method, which is based on the measurement of CO_2 , CO , and smoke aerosol. These represent the major carbon containing products of combustion for free burning. The concentrations of CO_2 and CO are relatively constant throughout the tests as shown in Figure 8. The CO_2 concentration in the stack, minus the background concentration equals 0.55% by volume which is a factor of 15 greater than the CO concentration. The mass concentration of carbon in the form of CO_2 , $M_c(\text{CO}_2)$, is obtained from the volume fraction of CO_2 , F_{CO_2} , with background subtracted, via the formula

$$M_c(\text{CO}_2) = F_{\text{CO}_2} \rho_{\text{CO}_2} (12/44) \quad (5)$$

The factor $(12/44)$ accounts for the carbon mass fraction of CO_2 and ρ_{CO_2} refers to the density of CO_2 within the instrument. A similar expression is obtained for $M_c(\text{CO})$. The mass fraction of carbon in the smoke aerosol is given by

$$f_s = M_s / (M_s + M_c(\text{CO}_2) + M_c(\text{CO})) \quad (6)$$

TABLE 1. SMOKE EMISSION AND PROPERTIES FOR 60 CM DIAMETER
PRUDHOE CRUDE POOL FIRE TEST NW35

<u>Property</u>	<u>Sample 1, 30 sec.^a after ignition</u>	<u>Sample 2, 230 sec. after ignition</u>	<u>Sample 3, 335 sec. after ignition</u>
dQ/dt, kW	153	186	181
ϵ_2	0.72×10^{-1}	0.80×10^{-1}	0.87×10^{-1}
F_{CO_2} , Vol. fraction ^b	0.46×10^{-2}	0.55×10^{-2}	0.54×10^{-2}
F_{CO} , Vol. fraction	0.26×10^{-3}	0.34×10^{-3}	0.36×10^{-3}
K_s , m ² /g	9.30	8.84	8.25
M_s , g/l ^{3 c}	0.217×10^{-3}	0.293×10^{-3}	0.312×10^{-3}

^aThe filter samples are collected for 1 minute and the properties listed in column 1 are averaged over this time interval.

^bThe background CO₂ concentration has been subtracted.

^cSmoke concentration corrected to ambient conditions.

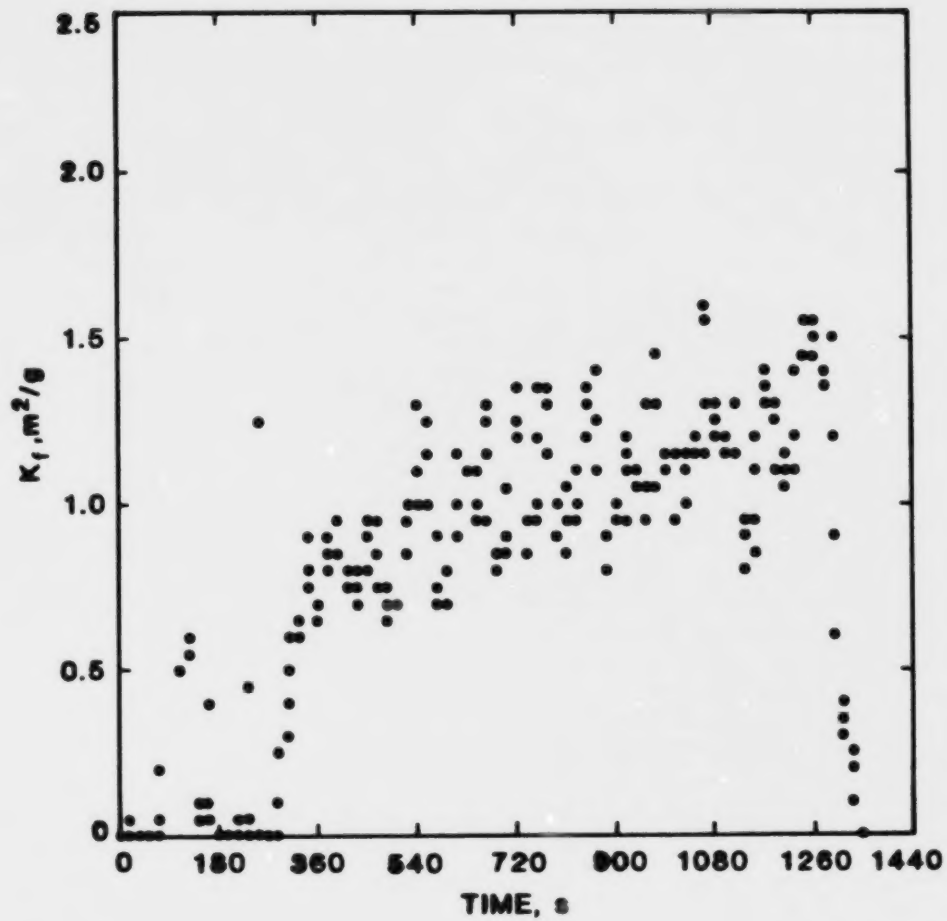


FIGURE 7. SPECIFIC EXTINCTION COEFFICIENT RELATIVE TO FUEL FOR PRUDHOE BAY CRUDE OIL BURNED IN A 0.4 METER DIAMETER POOL.

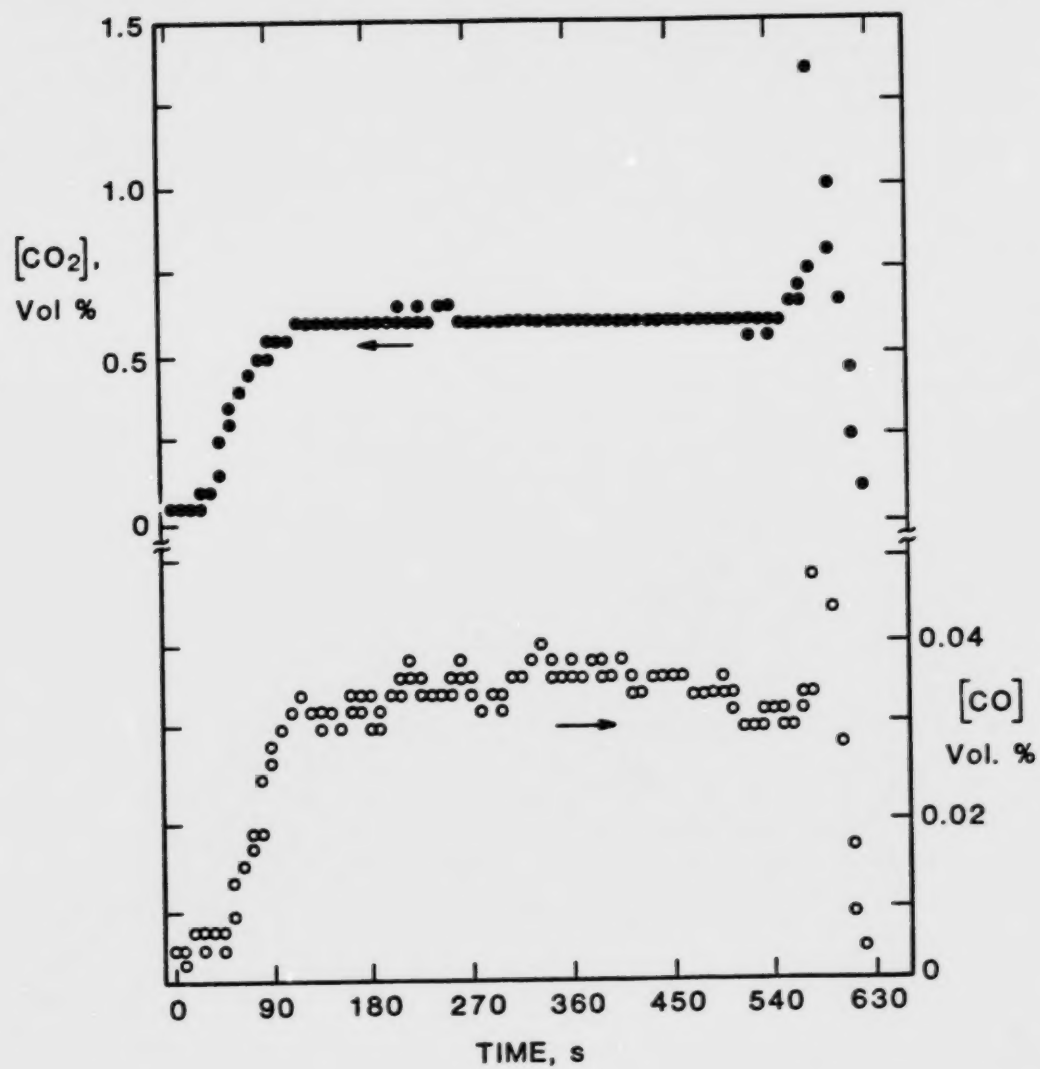


FIGURE 8. CO₂ AND CO CONCENTRATIONS FOR PRUDHOE BAY CRUDE OIL BURNED IN 0.6 METER DIAMETER POOL.

Finally, we obtain ϵ_2 by multiplying F_s by the carbon mass fraction of the fuel, F_c .

$$\epsilon_2 = f_s F_c \quad (7)$$

Lacking data on F_c for Prudhoe Bay crude oil, we have taken F_c to be 0.86, which is at the upper range for elemental carbon in crude oils. A slight overestimate is obtained in this analysis since the smoke is assumed to be 100% carbon. One might also expect a slight contribution from the hydrocarbon gases. Overall, we expect that these approximation will affect the final result by less than 5%.

As an example, for Sample 1 from Test NW35 (Table 1), we calculate the mass fraction of carbon in the form of CO_2 , CO , and smoke aerosol. First eq. (5) is used to calculate the mass concentration of carbon corresponding to the volume fractions F_{CO_2} and F_{CO} in Table 1. The density of CO_2 and CO under test conditions is computed from the ideal gas law as:

$$\rho_{\text{CO}_2} = \frac{44P}{RT}; \quad \rho_{\text{CO}} = \frac{28P}{RT} \quad (8)$$

For Test NW35 (Table 1) $P = 0.976$ atmospheres, and $T = 295$ K. The appropriate gas constant R is 0.082 liter-atm/gmole/K. The mass fraction of carbon in the smoke aerosol is obtained from eq. (6). The mass fractions of CO_2 and CO are also obtained from eq. (6) with M_s in the numerator replaced by $M_c(\text{CO}_2)$ and $M_c(\text{CO})$, respectively. The results are 0.867 of carbon in the form of CO_2 , 0.049 as CO and 0.084 as smoke aerosol.

Size Distribution

Samples collected from the seven stages and backup filter of the cascade impactor are shown in Figure 9. The first impaction stage is a single relatively low velocity nozzle, which impacts out particles with aerodynamic diameters greater than 13 μm . With each successive stage, smaller and smaller particles are impacted out as indicated by the particle size cutoffs in Figure 9. The fact that the size distribution is very wide is indicated by the smoke aerosol deposition on each stage.

The quantitative results regarding the size distribution function are shown in Figure 10. The cumulative aerodynamic size distributions are plotted for data obtained from two 60 cm Prudhoe Bay crude oil burns. In both cases, about 20 mg of smoke aerosol were collected on the impaction stages plus backup filter. Since the plot in Figure 10 is on log-probability paper, the straightline fit to the data indicates that the mass distribution is log-normal. The mass median diameter, the 50% point in terms of mass, is found to be 0.5 μm for both experiments. The geometric standard deviation, σ_g , for the size distribution is obtained from the relation

$$\sigma_g = D(84.1\%)/D(50\%) \quad (9)$$

We find σ_g equal 7.1 and 6.4 for the 60 cm pool burns on test number NW35 and test number NW36, respectively. For a log-normal distribution [7] 67% of the aerosol mass is in the particle diameter range $\log D_{50} \pm \log \sigma_g$; for $D_{50} = 0.50 \mu\text{m}$ and $\sigma_g = 7.1$, this corresponds to the size range 0.07–3.55 μm . This represents a very broad size distribution.

The complexity of the particle structure is indicated by the transmission electron micrographs in Figures 11 and 12. It is seen that the particles have

TABLE 2. SUMMARY OF SMOKE EMISSION DATA FOR 40 AND 60 CM DIAMETER
PRUDHOE CRUDE POOL FIRES

<u>Property</u>	<u>Test NW33</u> <u>40 cm pool</u>	<u>Test NW34</u> <u>40 cm pool</u>	<u>Test NW35</u> <u>60 cm pool</u>	<u>Test NW36</u> <u>60 cm pool</u>	<u>Average</u>
dQ/dt, kW	63	61	173	178	
dm/dt, g/s	1.81	1.75	-	-	
ϵ_1	0.107	0.096	-	-	
ϵ_2	0.098	0.079	0.080	0.090	0.087 ± 0.009
F_{CO_2} , Vol. fraction	0.15×10^{-2}	0.18×10^{-2}	0.52×10^{-2}	0.53×10^{-2}	
F_{CO} , Vol. fraction	-	-	0.32×10^{-3}	0.32×10^{-3}	
K_g , m^2/g	8.95	10.00	8.80	8.64	9.10 ± 0.61
K_f , m^2/g	0.96	0.96	-	-	
D_m , μm	0.74	0.62	0.50	0.50	
σ	5.8	6.4	7.1	6.4	

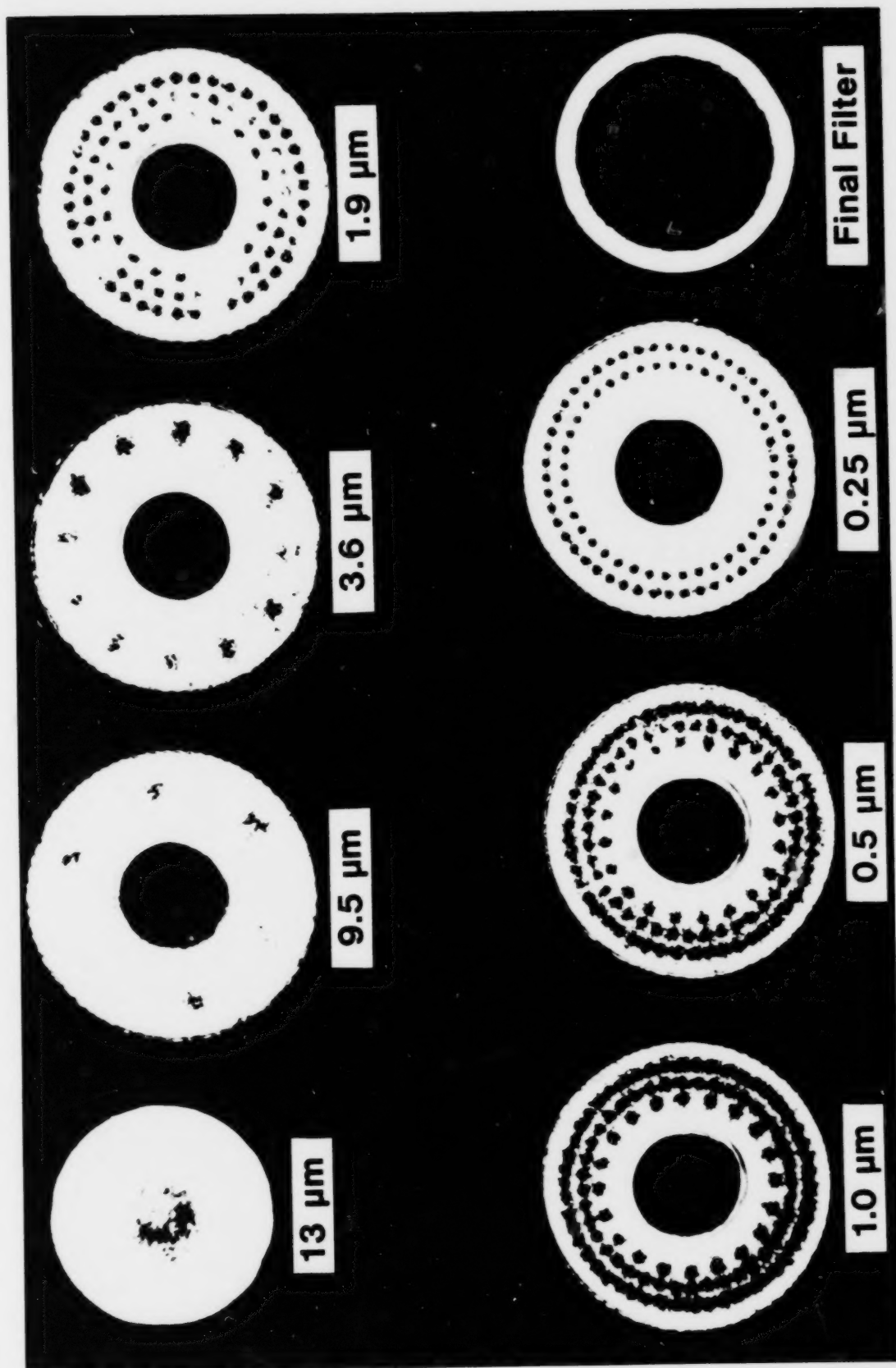


FIGURE 9. SMOKE AEROSOL DEPOSITION ON SEVEN STAGES AND BACKUP FILTER OF CASCADE IMPACTOR FROM 0.6 METER DIAMETER PRUDHOE BAY CRUDE OIL POOL FIRE.

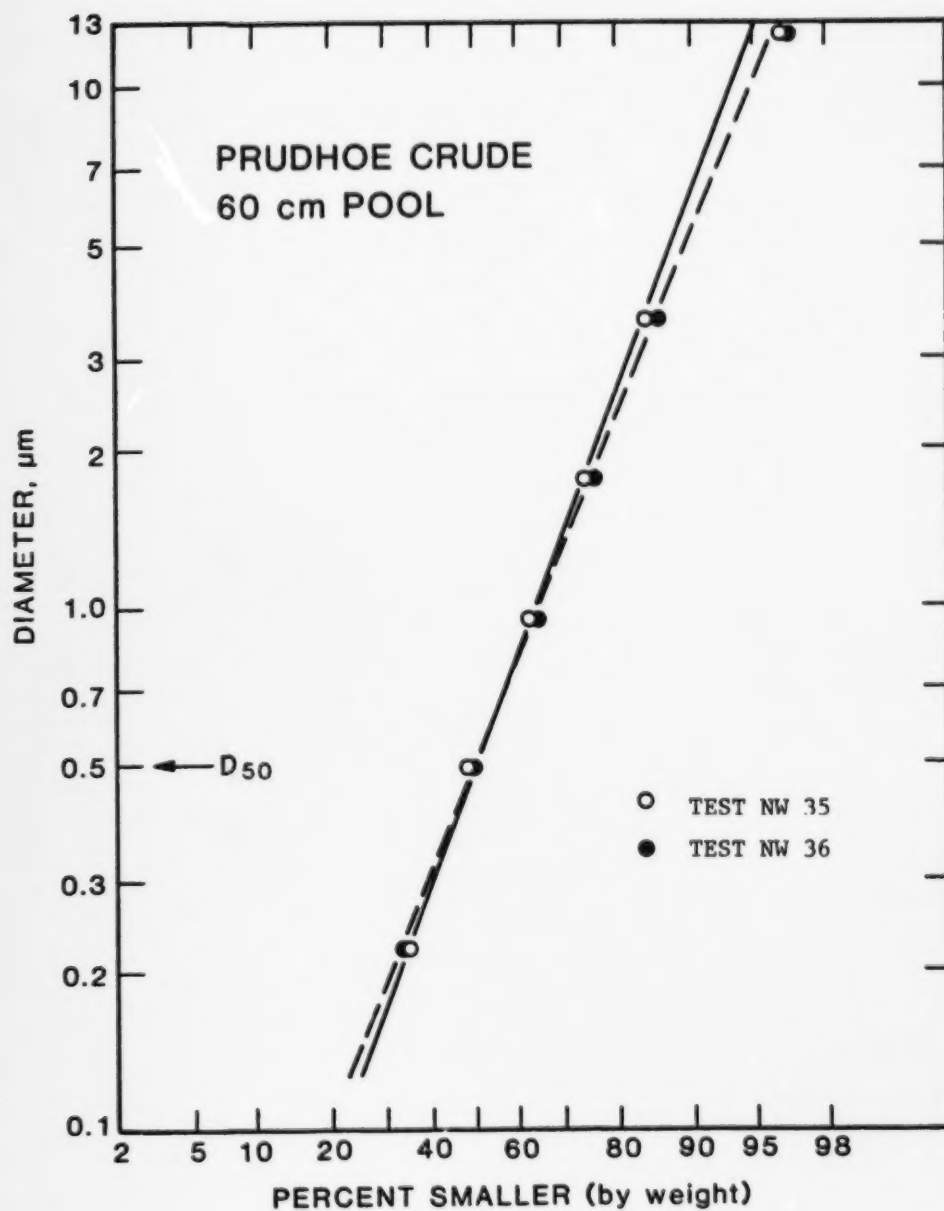


FIGURE 10. CUMMULATIVE AERODYNAMIC SIZE DISTRIBUTION OF SMOKE AEROSOL PRODUCED BY 0.6 METER DIAMETER PRUDHOE BAY CRUDE OIL POOL FIRE.



FIGURE 11. ELECTRON MICROGRAPH OF SMOKE PARTICLES PRODUCED BY 0.6 METER DIAMETER PRUDHOE BAY CRUDE OIL POOL FIRE, 3 MICROMETER SCALE.

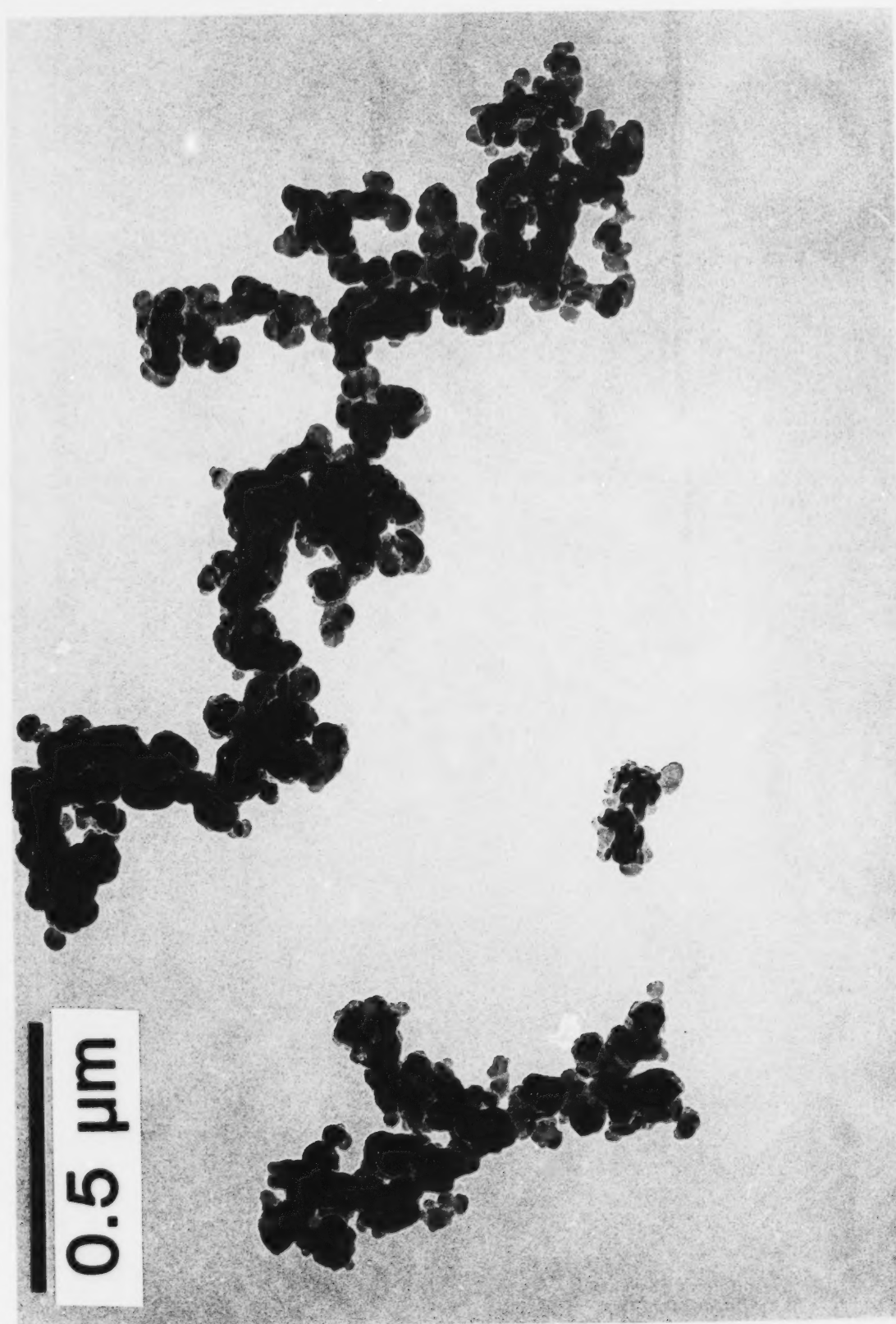


FIGURE 12. ELECTRON MICROGRAPH OF SMOKE PARTICLES PRODUCED BY 0.6 METER DIAMETER PRUDHOE BAY CRUDE OIL POOL FIRE, 0.5 MICROMETER SCALE.

a low density agglomerate structure made up of many small spherules in the size range 0.02-0.06 μm . As is apparent from Figure 11, there is a wide range in cluster size.

Discussion

A summary of the results from four pool burns is given in Table 2. Increasing the pool size from 40 to 60 cm more than doubles the heat release rate and the mass loss rate of fuel, but it has a relatively minor effect on the smoke conversion factor and in the smoke properties. The emission of smoke is high with ϵ about 0.10 (10% conversion to smoke) and the specific extinction coefficient, $K_s = 9.1$, is similar to what has been observed for other soot producing fuels. Over 50% of the smoke aerosol is in the submicrometer aerodynamic size range, which is indicative of a long atmospheric residence time and potentially high deposition in the lower respiratory tract.

One of the most striking features of the burning oil is the very rapid combustion over the final thirty seconds. There are qualitative indications that the smoke aerosol produced under these conditions has a significant tarry component not seen in the smoke collected during the steady combustion phase. This is potentially an important effect since the thickness of the oil layer resulting from a spill may be relatively small compared to the initial thickness in the test fires of 0.27 m. A significant fraction of the total smoke emitted from combustion of an oil spill originate from the intense burning phase.

The fact that we do not see any significant scale effect in regard to smoke emission may simply be a result of the relatively narrow range of scales studied. An increase by a factor of 10 to 100 in burning rate may have a significant effect on the smoke aerosol emission and smoke properties.

The smoke aerosol collection and characterization has been carried out at elevated temperatures around 100°C. Without further study, one can not be certain whether the results are directly applicable to diluted, aged smoke aerosol that would be characteristic of smoke far downwind of actual fires.

BURN RESIDUE COMPOSITION

The burning effects on the composition of Prudhoe Bay crude oil was examined by comparative ^{13}C NMR spectroscopy [8] between fresh oil and the burn residue. Of specific interest was the fate of the lighter fractions, which include the short-chain alkanes, cycloalkanes, and substituted benzenes.

The ^{13}C NMR spectra were collected at 100 MHz with proton decoupling and nuclear Overhauser enhancement. Solutions of crude oil and burned crude oil were 50% by volume in deuterochloroform.

The principal peaks in the aliphatic region of the crude oil spectrum are assigned in Figure 13 to either chain-ending carbons (C_1 through C_4) or chain-interior carbons (C_i) in alkanes. Their relative intensities reflect the distribution of alkane chain lengths. Upon burning, the C_1 through C_4 intensities are uniformly attenuated in relationship to the intensity of C_i . This result is interpreted as a selective depletion of short chain alkanes in the burned crude. A similar fate is indicated for the cycloalkanes. Their resonances, which are marked with asterisks (Fig. 13), are either absent from or attenuated in the spectrum of the burned crude. Evidence of burning effects is much more dramatic in the aromatic region (Fig. 14) of the crude oil spectra. The sharp signals in Figure 14, which are due mainly to mono-ring aromatics including benzene, toluene, and xylenes, are for the most part absent in the burned crude spectrum (Fig. 14).



FIGURE 13. A COMPARISON OF THE ALIPHATIC REGION OF THE ^{13}C NMR SPECTRA OF (A) PRUDHOE BAY NORTH SHORE CRUDE OIL, AND (B) BURN RESIDUE OF PRUDHOE BAY NORTH SHORE CRUDE OIL.

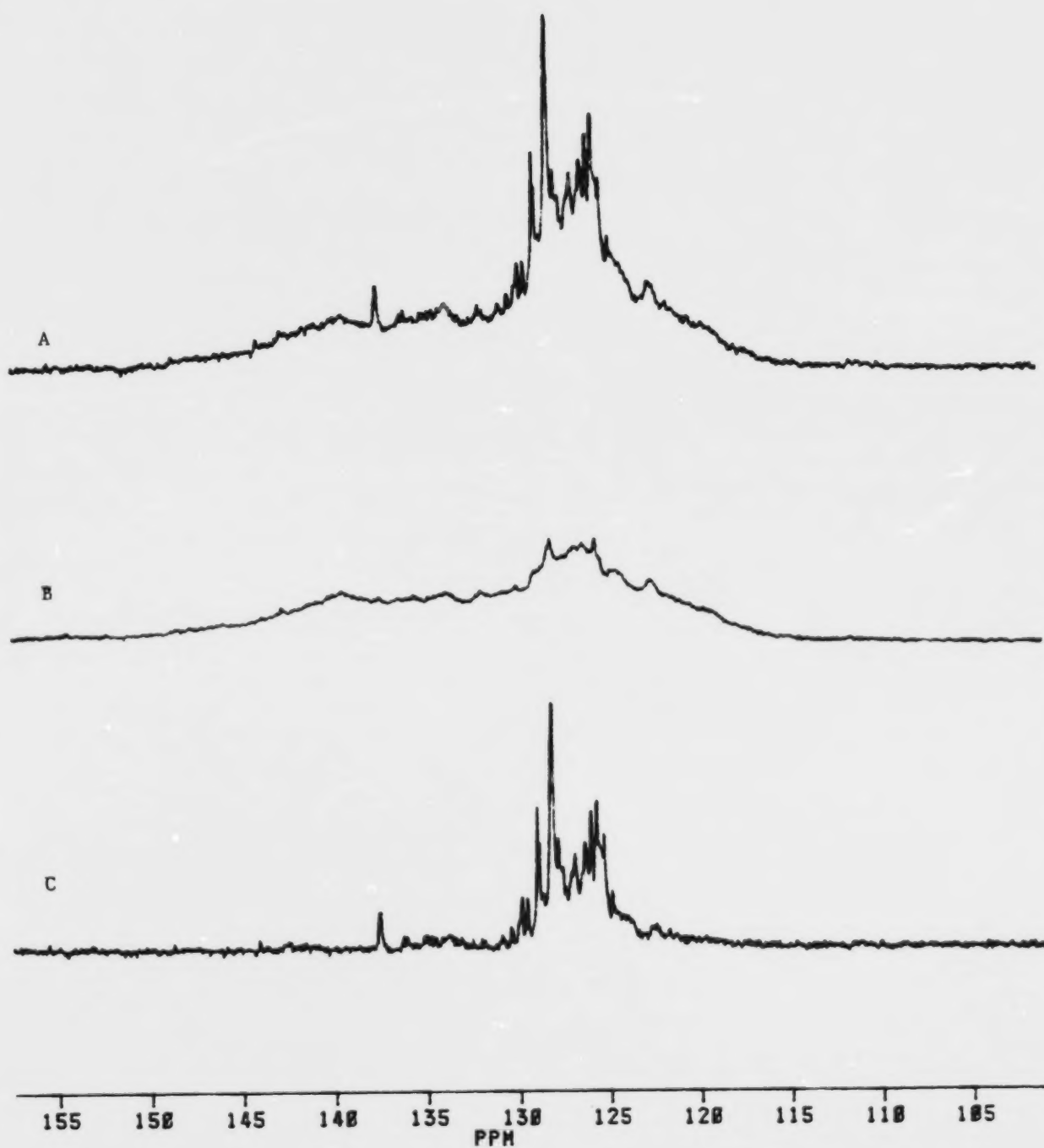


FIGURE 14. A COMPARISON OF THE AROMATIC REGION OF THE ^{13}C NMR SPECTRA OF (A) PRUDHOE BAY NORTH SHORE CRUDE OIL, (B) BURN RESIDUE OF PRUDHOE BAY NORTH SHORE CRUDE OIL, AND (C) THE DIFFERENCE (A-B), BROAD BAN RESONANCES WERE NORMALIZED TO EQUAL INTENSITY.

A more quantitative examination of the depletion of specific alkanes and cycloalkanes would require a combination of gravimetric and ^{13}C NMR analyses of distillation fractions. This type of analysis is being planned.

CALCULATION OF INDUCED AIR FLOW

In recent years there has been an interest in determining if it is possible for fire induced air flows into large fires to cause a migration of the oil spill towards the burning area. Large oil burns on water have been conducted to measure this induced surface air flow [9]. These experiments, although carefully conducted, are hard to interrupt because of non-ideal conditions encountered in field testing such as uncontrolled ambient winds. It is also known, particularly in the case of oil spills, that clean-up will require the ignition of many relatively small patches of oil that are separated by either open water or layers of oil too thin to ignite.

This part of the study details a calculation of induced wind into an area containing randomly distributed fire sources having various steady energy release rates. Present calculations do not include any interaction between the induced flow and the surface. A sample calculation of the induced air flow velocity field 0.8 m above the surface over an area 100 m x 100 m containing 20 fires ranging in energy release rate from 200 kW to 3.2 MW was performed. Based on the measured energy release rate for Prudhoe Bay crude oil in a 0.6 m diameter pool of 640 kW/m² these fires would represent crude oil pools ranging in diameter from 0.63 m to 2.5 m.

The Model for Fire Induced Flow

The flow induced by an oil spill fire is primarily determined by three factors: the geometrical arrangement of the burning parcels of fuel, the rate of heat released by each individual fuel element, and the atmospheric environment in the neighborhood of the spill. In any given spill scenario, there is a considerable amount of randomness in each of these factors. The mathematical model described below attempts to deal with this situation by combining random distributions of location and burning rate of the individual patches of fuel with a deterministic description of the composite flow generated by a given realization of the spill scenario. Each patch of burning oil is assumed to be sufficiently removed from the others so that the buoyant plume of hot gas and smoke rising above the patch evolves independently. Under these circumstances, the composite flow field can be decomposed into a collection of individual flows associated with each plume. The flow pattern associated with a single plume is then analyzed in detail and the results compared with experimental data. The process by which the composite flow is calculated is then outlined; and the induced surface wind for a sample distribution of plumes is displayed.

The starting point is the inviscid equations of fluid mechanics which control the large scale fluid motion of interest. These laws, expressing conservation of mass, momentum, energy, and an equation of state, respectively are:

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \vec{u} = 0$$

$$\rho \frac{D\vec{u}}{Dt} + \nabla \tilde{p} - (\rho - \rho_0) \vec{g} = 0$$

$$\rho C_p \frac{DT}{Dt} = Q(\vec{r}, t) \quad (10)$$

$$P_0 = \rho_0 RT$$

Here P , ρ , $\vec{u}$, and T are, respectively, the local pressure, density, velocity, and temperature in the gas at position $\vec{r}$ and time t induced by a rate of energy release $Q(\vec{r}, t)$. The gas has a specific heat C_p and gas constant R , while $\vec{g}$ is the gravitational acceleration. The quantities P_0 and ρ_0 are sea level ambient pressure and density, while $\tilde{p}$ represents the small perturbation from hydrostatic pressure that drives the motion. All plumes are assumed to evolve in uniform atmosphere at rest far from the plumes. The convective operator D/Dt includes local time dependence:

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \vec{u} \cdot \nabla$$

It is certainly not feasible to contemplate solving eq. (10) directly. Instead, we make use of two equivalent results. If the first of eq. (10) is multiplied by C_p and added to the third and the equation of state is used, the divergence of the velocity field can be expressed as:

$$\nabla \cdot \vec{u} = Q(\vec{r}, t) / \rho_0 C_p T_0 \quad (11)$$

Physically, eq. (11) states that the volumetric expansion rate of any fluid element is proportional to the net rate of heat addition. It is important to note that although the heat is added to the atmosphere only in the vicinity of each patch of burning fuel, eq. (11) is valid everywhere above the surface.

The second result needed is Bjerknes theorem [10]. The fluid vorticity $\vec{\omega}$ is defined in terms of the fluid velocity $\vec{u}$ as:

$$\nabla \times \vec{u} \equiv \vec{\omega} \quad (12)$$

Now consider a closed loop of Lagrangian marked particles moving with the local fluid velocity. The circulation Γ around that closed loop is defined as:

$$\Gamma \equiv \oint_{\ell} \vec{u} \cdot d\vec{r} = \oint \vec{\omega} \cdot \vec{n} dA \quad (13)$$

Here $\vec{n}$ is a unit vector normal to any surface A bounded by the closed loop ℓ of marked particles. The momentum conservation equation, the second of eq. (10), can then be manipulated into the form:

$$\frac{d\vec{r}}{dt} = \oint_{\ell} \{ [(\rho - \rho_0) / \rho_0] \vec{g} - \nabla \tilde{p} / \rho \} \cdot d\vec{r} \quad (14)$$

Equation (14) is Bjerknes theorem. Physically, it states that vorticity can be created in a fluid away from a boundary only through the mechanism of density gradients. In the absence of such gradients the circulation around the closed loop, and hence the vorticity contained within the loop, cannot change.

Now consider the history of a fluid element originating from rest far from any of the plumes generated by the oil spill fire. Initially the fluid contained no vorticity, and in its approach to the fire it remains irrotational. As it enters one of the smoke plumes it encounters large density gradients, and an intense vortex field is created. Thus, eq. (12) can be rewritten as:

$$\nabla \times \vec{u} = \vec{\omega}_p(\vec{r}, t) \quad (15)$$

Here, $\vec{\omega}_p$ denotes the vorticity in the plumes. Just as in the case of eq. (11), eq. (15) holds everywhere even though $\vec{\omega}_p$ only involves the velocity gradients inside the plumes.

Two further points should be noted. First, since the right hand sides of eqs. (11) and (15) involve only information inside the plumes, if the plumes remain distinct we can write:

$$\begin{aligned} Q(\vec{r}, t) &= \sum_i Q_i(\vec{r}, t) \\ \vec{\omega}_p(\vec{r}, t) &= \sum_i \vec{\omega}_{pi}(\vec{r}, t) \end{aligned} \quad (16)$$

Here the sum is taken over each individual plume. Thus, a velocity field $\vec{u}_i$ can be associated with each plume, where the velocity field is the solution to

$$\begin{aligned} \nabla \cdot \vec{u}_i &= Q_i / \rho_o C_p T_o \\ \nabla \times \vec{u}_i &= \vec{\omega}_{pi} \end{aligned} \quad (17)$$

Second, these formulae are valid both instantaneously and in a time averaged sense. If time dependent information about the structure of an individual fire plume is available, then it can be used in eq. (17). At present, only time averaged information is available. In either case, the kinematics of a general vector field insures that a knowledge of the divergence and curl of the vector is sufficient to determine it everywhere uniquely.

The physical information available on the time averaged structure of fire plumes has been analyzed by McCaffrey [11]. He notes that there is ample experimental support for a Gaussian radial distribution of the mean vertical velocity in the plume. This can be expressed analytically in the form:

$$u = U(Z) \exp \left\{ - \left[r/R(Z) \right]^2 \right\} \quad (18)$$

Here u is the vertical velocity component, $U(Z)$ its value on the center-line of the axially symmetric plume, and $R(Z)$ the mean plume width. The variable Z is the height above the sea surface and r is the radial distance from the plume centerline. McCaffrey furnishes an analytical correlation of the experimental data for $U(Z)$ and the centerline temperature. By enforcing the

requirement for energy and momentum conservation on average across the plume at each height Z , he is able to infer the mean radius $R(Z)$. Using eq. (18) and the fact that the time average plume is axially symmetric, the vorticity ω can be inferred as:

$$\begin{aligned}\vec{\omega} &= \omega_{\phi} \vec{\phi} \\ \omega_{\phi} &\approx [2U(Z)/R(Z)] \{r/R \exp [-(r/R)^2]\}\end{aligned}\quad (19)$$

The quantity $\vec{\phi}$ is a unit vector in the azimuthal direction.

The detailed form of the centerline velocity correlation will be shown below. For the moment, the most important aspect of the correlation is the scaling law implied by the overall conservation of energy in each plume. If Q_i is the total rate of energy release into an individual fire plume, then the velocity field induced by that fire depends on a single length scale D_i , defined as:

$$D_i = (\hat{Q}_i / \rho_o C_p T_o \sqrt{g})^{2/5} \quad (20)$$

Moreover, the velocity field $\vec{u}_i$ must be of the form:

$$\begin{aligned}\vec{u}_i &= (gD_i)^{1/2} \vec{u}_* (\vec{r}_*) \\ \vec{r}_* &= \vec{r}/D_i\end{aligned}\quad (21)$$

Thus, a single dimensionless velocity $\vec{u}_*$ can be calculated from eqs. (17) and (19) which is valid for a fire of any strength. Given the dimensionless result $\vec{u}_*$, the physical velocity field for a given fire strength can be determined from eqs. (20) and (21).

The details of the calculation of the universal dimensionless velocity $\vec{u}_*$ will be omitted here. However, the resulting mean streamline pattern is shown in Figure 15. The flow enters nearly horizontally from the right, then turns abruptly upwards as it enters the plume. The approximate plume boundary is moving slowly to the right, growing nearly linearly with increasing height. The relatively close spacing of the streamlines after they enter the plume indicates the high velocities present in the plume. Figure 16 shows the ground level radial inflow velocity induced by the plume. The inflow velocity has two components. The dotted line denoted $U_r(\psi)$ represents the very strong inflow induced by the vorticity in the plume. The dashed line denoted $U_r(\phi)$ represents a weak outflow due to the volumetric expansion associated with the heat released in the flames at the base of the plume. The solid line is the net radial inflow. The peak value corresponds to a location near the outer edge of the flame zone at the base of the plume.

These results can be checked against experimental data in two stages. Figure 17 shows the calculated centerline vertical velocity, the upper solid line, plotted as a function of height. The lower solid line is the dimensionless centerline correlation developed by McCaffrey, based on measurements of laboratory scale fires. The agreement is quite good; the maximum discrepancy between the two curves is about four percent. The calculated velocity is further broken down into the vorticity and expansion induced components, denoted as before by dotted and dashed lines, respectively. Figure 18 shows the correlation compared with experimental data taken from a variety of large scale pool fires. The velocity correlation is replotted in the middle curve. The data, though relatively sparse, tracks the correlation quite well.

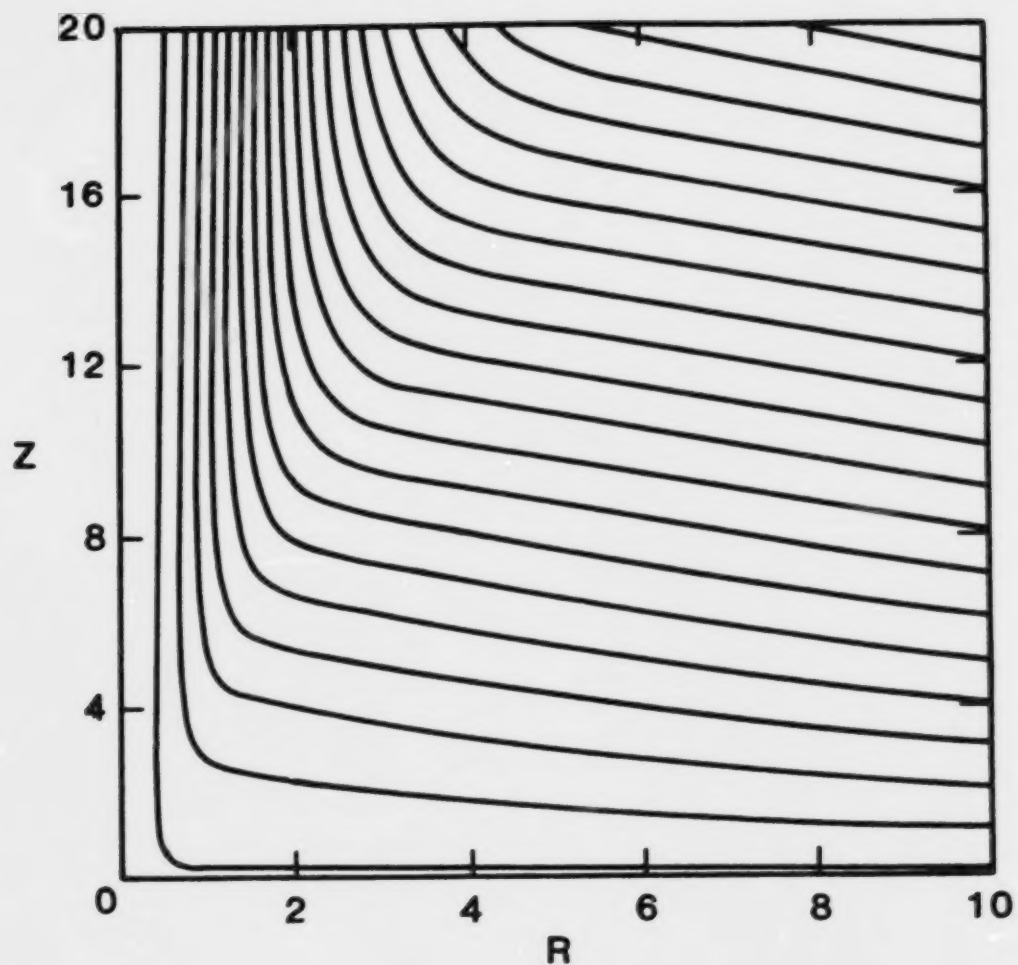


FIGURE 15. TIME AVERAGED STREAMLINES CALCULATED FROM DIMENSIONLESS VELOCITY FIELD IN TERMS OF SCALED RADIAL (R) AND VERTICAL (Z) COORDINATES.

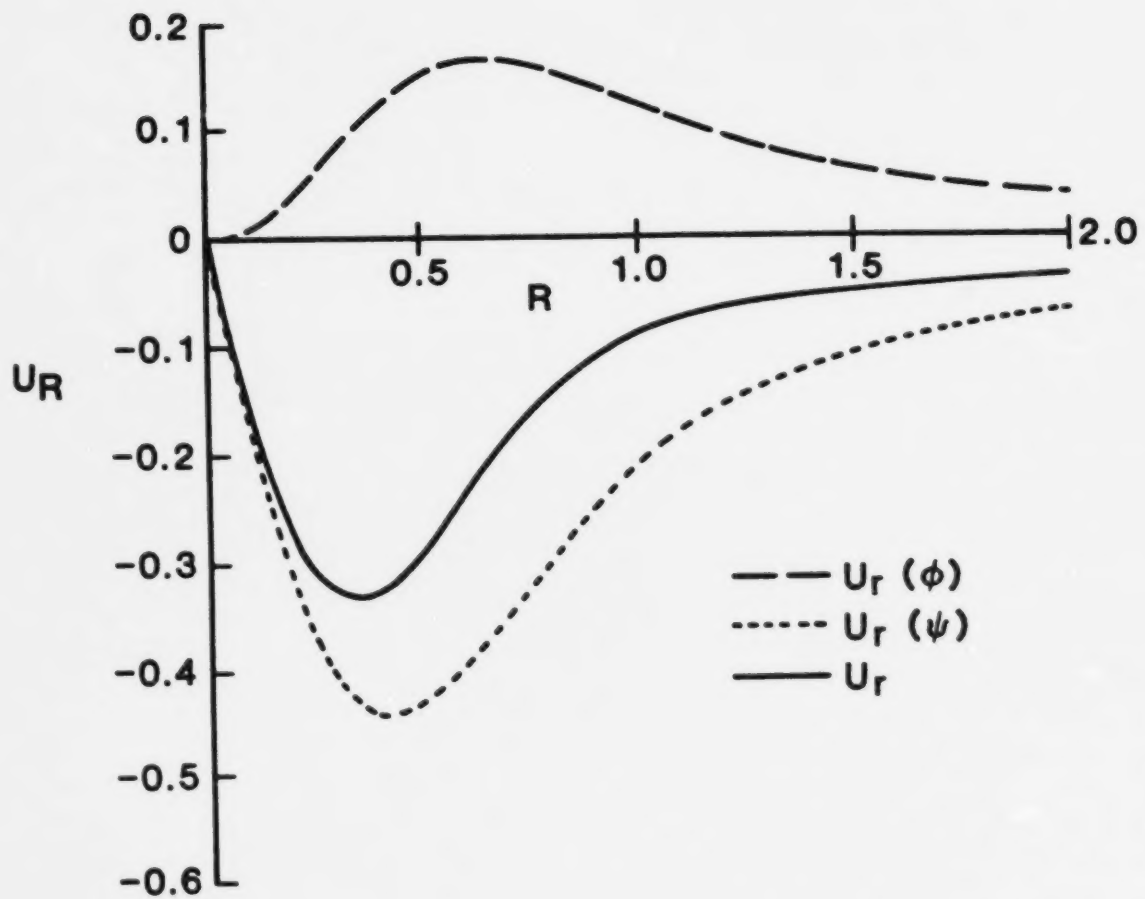


FIGURE 16. GROUND LEVEL RADIAL INFLOW SHOWING VORTICITY INDUCED FLOW $U_r(\psi)$, VOLUMETRIC EXPANSION OUTFLOW $U_r(\phi)$, AND NET INFLOW U_r .

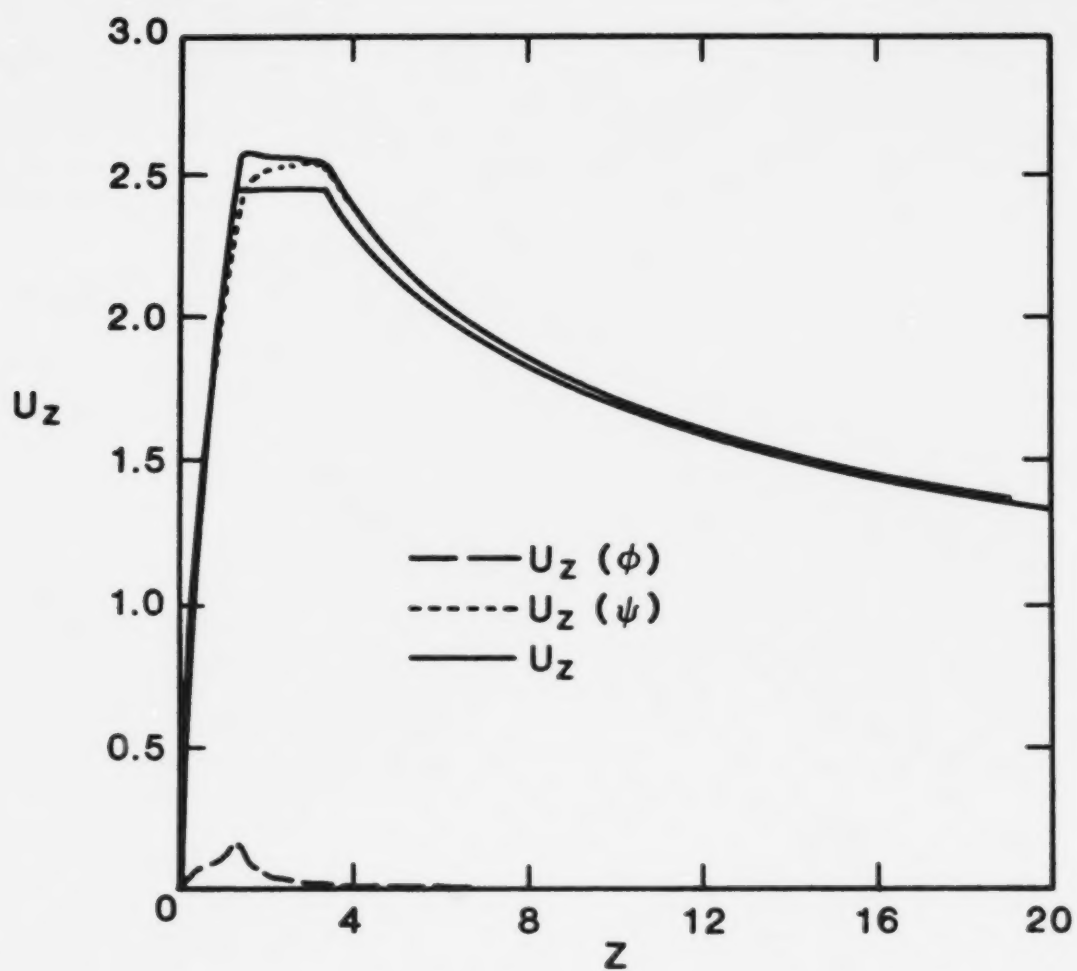


FIGURE 17. VERTICAL PLUME CENTERLINE VELOCITIES SHOWING TOTAL CALCULATED VELOCITY (UPPER SOLID LINE), DATA CORRELATION (LOWER SOLID LINE), VORTICITY INDUCED FLOW $U_z(\psi)$ AND VOLUMETRIC EXPANSION FLOW $U_z(\phi)$.

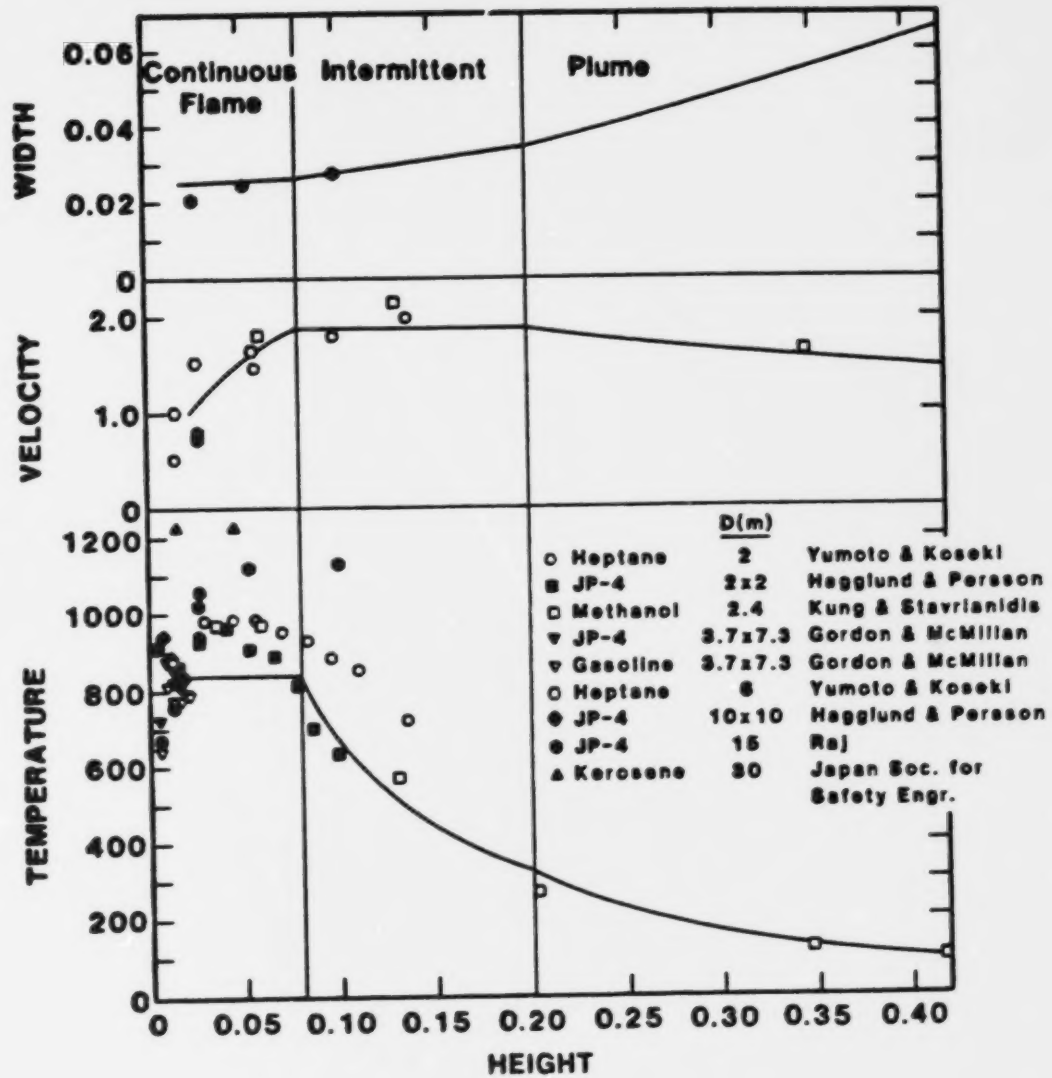


FIGURE 18. COMPARISON OF CENTERLINE TEMPERATURE, VELOCITY, AND GAUSSIAN PLUME WIDTH CORRELATIONS WITH LARGE SCALE POOL FIRE DATA.

Given the non-dimensional solution for the flow induced by a single fire, we now turn to the calculation of the composite flow. The individual plume flow pattern is symmetric about a vertical axis centered above the patch of burning fuel. However, an assemblage of such flows, each with an axis of symmetry in a different location, is inherently three dimensional. Moreover, allowance must be made for the fact that the fires can vary widely in strength. In order to proceed, it is necessary to make some assumptions about location and fire strength. In practice very little information is likely to be available about an oil spill event other than the approximate area covered and the amount of fuel released and burning. Accordingly, a computational scheme is set up which distributes a prescribed number of fires into five discrete strength ranges, each rate of energy release a factor of two larger than that which precedes it. In the absence of any better information, the probability distribution is taken to be uniform with respect to fire strength. Each of the fires is then distributed randomly into an overall rectangular area which is prescribed. The composite velocity near water level is then calculated on a uniform 100 x 100 grid within the spill area.

SAMPLE CALCULATION

A sample calculation is shown in Figure 19. Twenty plumes ranging in strength from 200 kW to 3.2 MW (see Table 3) are randomly introduced into a square 100 meters on a side. Velocity vector arrows of length proportional to the magnitude of the local velocity field are introduced at 5 meter intervals. Contours of constant dimensionless speed are also shown as an aid to locating the burning areas. The areas where the speed contours cluster tightly together indicate the location of the individual fires. The velocities are actually calculated at a height about 0.8 m above the surface. The coordinates and velocities are normalized with respect to the scaling laws introduced in eqs. (20) and (21). The largest individual fire of strength 3.2 MW is used in the non-dimensionalization. The maximum velocity visible at this resolution scale (Figure 19) is approximately 0.8 m/sec. The tick marks on the boundaries are spaced at 1 meter intervals.

Figure 20 shows a local detail magnified ten times in each direction centered near the large fire 3.2 MW (fire #19) about 2/3 of the way to the right and 1/5 up from the bottom of Figure 19. At this resolution, the inflow into the fire plume is clearly visible. Since it is possible to resolve the flow nearer to the plume, the maximum velocity in the fine grid approaches the dimensionless peak inflow velocity for an individual plume U_r in Figure 16. The peak velocity shown in Fig. 20 is about 1.1 m/sec.

Calculations of this type may be extended using idealized wind conditions and measured soot properties to predict convection of the soot produced by the oil spill fires. Basic studies related to the formulation of this more advanced model are presently underway.

TABLE 3. DISTRIBUTION OF FIRE ENERGY RELEASE RATES AND EQUIVALENT PRUDHOE BAY CRUDE OIL POOL FIRE DIAMETERS USED IN FIGURE 19

Fire No.	Location X Unit from Left Border (Fig. 19)	Location Y Units from Bottom Border (Fig. 19)	Energy Release Rate kW	Equivalent Pool Diameter m
1	96.613	14.762	200	0.63
2	40.852	61.420	1600	1.78
3	5.483	92.562	200	0.63
4	8.217	29.148	1600	1.78
5	94.120	49.268	800	1.26
6	52.152	89.503	1600	1.78
7	86.683	46.312	3200	2.52
8	39.632	55.463	1600	1.78
9	13.900	2.955	400	0.89
10	33.547	44.622	200	0.63
11	71.857	90.247	200	0.63
12	41.348	22.350	3200	2.52
13	1.095	26.527	800	1.26
14	2.737	40.275	1600	1.78
15	48.530	86.992	800	1.26
16	28.918	32.567	400	0.89
17	74.675	39.835	1600	1.78
18	5.935	32.542	1600	1.78
19	68.680	21.433	3200	2.52
20	74.535	72.075	3200	2.52

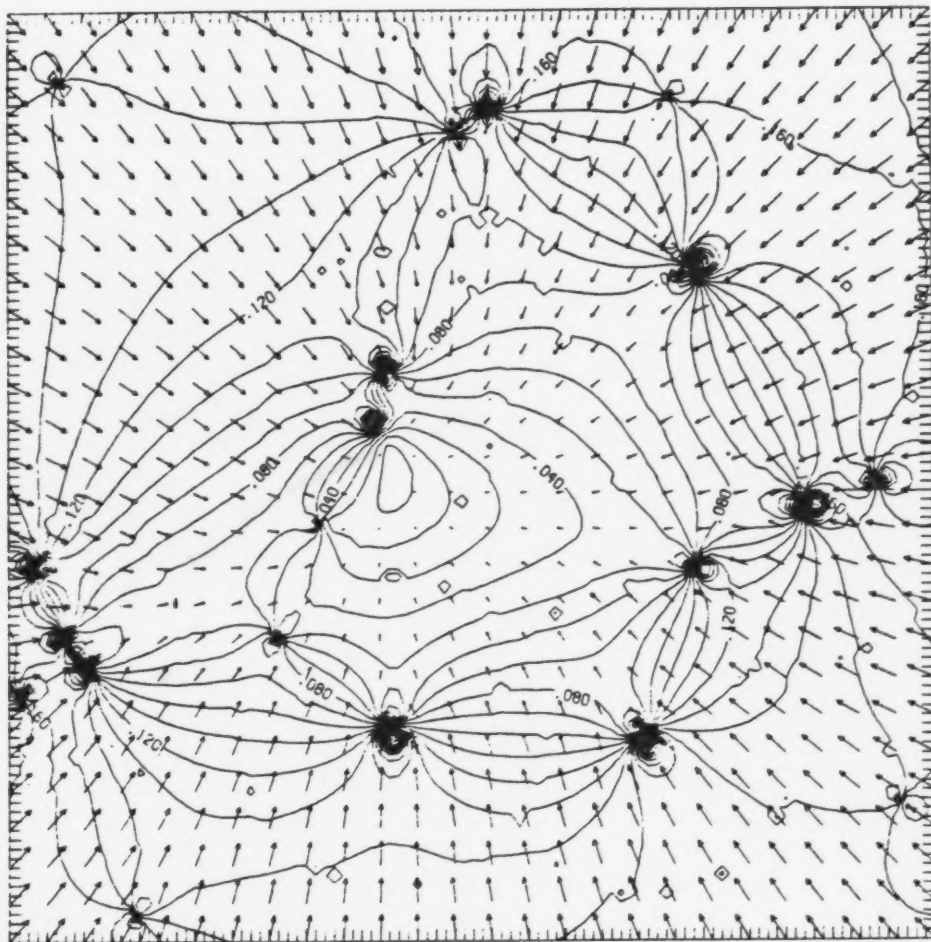


FIGURE 19. COMPOSITE SEA LEVEL INDUCED FLOW GENERATED BY TWENTY RANDOMLY DISTRIBUTED FIRES RANGING IN STRENGTH FROM 200 KILOWATTS TO 3.2 MEGAWATTS. THE OVERALL AREA IS 100 METERS ON A SIDE. VELOCITY RECTORS AND SPEED CONTOURS ARE SHOWN.

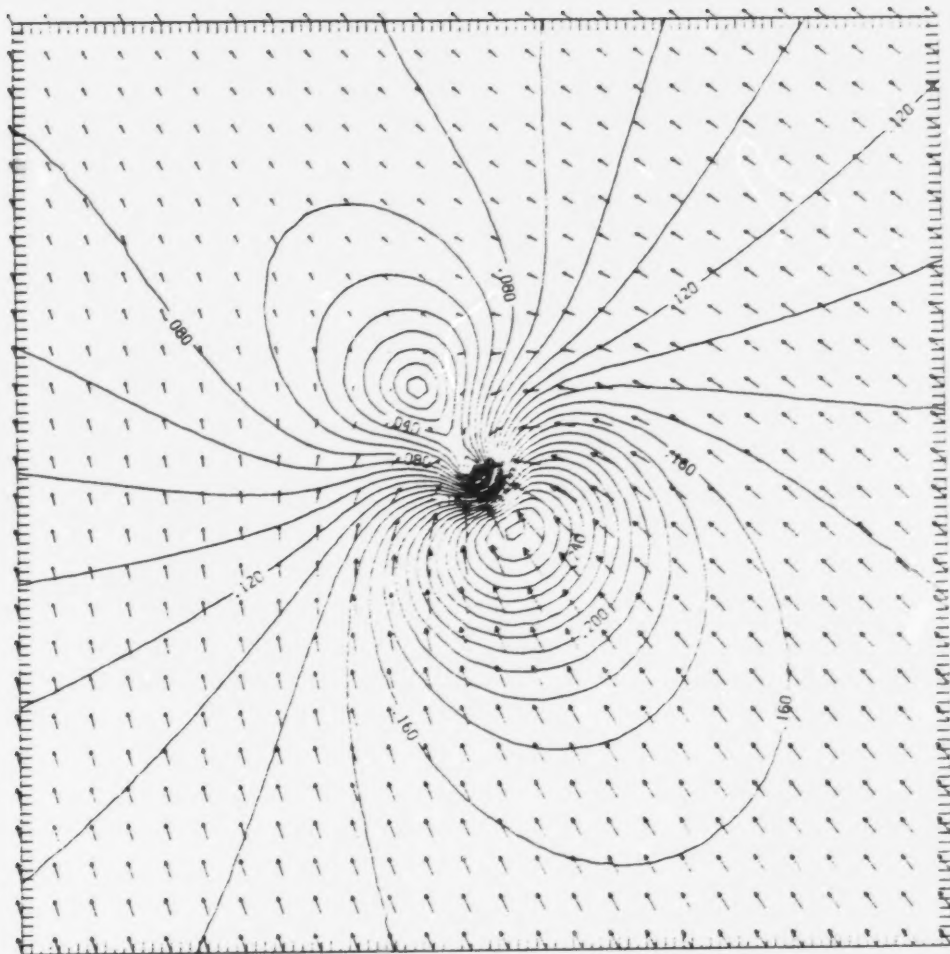


FIGURE 20. DETAIL OF VELOCITIES AND SPEED CONTOURS SHOWN IN FIGURE 19 CENTERED NEAR FIRE (FIRE #19, 3.2 MW) 2/3 TO THE RIGHT AND 1/5 UP FROM BOTTOM. SCALE MAGNIFIED 10 TIMES.

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THE USE OF OIL SPILL INCINERATORS
FOR THE DISPOSAL OF OIL BASED DRILLING MUDS

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ABSTRACT

This project investigated the possibility of using oil spill response equipment for tasks other than oil spill response. Four oil spill incinerators were used to dispose of oil based drilling muds. Three muds (one fresh diesel, one fresh mineral and one used mineral) were incinerated using the Air-Portable Incinerator, the Reciprocating Kiln, the Saacke Waste Oil Burner and the T.O.P.S. (Technical Offshore Petroleum Services) Burner. The efficiency of burn and quality of the resulting residue were evaluated for each device.

For each of the incinerators, it was found that all three muds could be burned with equal efficiency. The fact that a mud was fresh or used, mineral based or diesel based had no effect on its ability to burn. Two burners proved to be particularly useful for burning oil based muds. The T.O.P.S. burner burned all muds at high rates of combustion (average 331 bbls/day). The Saacke burner also provided significant burning capability (average 166 bbl/day) although this unit would require modification to handle the solids content on a continuous basis. The Air Portable Incinerator and Reciprocating Kiln both provided effective means of disposal although the low throughput of these two devices would limit their operational use.

INTRODUCTION

The Canada Oil and Gas Lands Administration (COGLA) is preparing guidelines on the use of oil based drilling muds for offshore exploration and production. A prime topic of discussion has been the possible disposal options of oil based muds following their use. It was generally agreed that incineration may be a feasible means of disposal. This technique may be appropriate for areas of operation which have easy access to incinerator facilities; however some frontier areas (eg. Beaufort Sea, High Arctic, Labrador coast) do not have such incinerators available. Transportation and handling costs to bring the mud to the incinerator could be prohibitive and this disposal technique would not be applicable in those areas.

Dome Petroleum utilizes a number of specialized incinerators for use at oil spill sites in the Arctic. These devices were designed to be highly mobile, to be used in remote areas, to require minimal support facilities, and to be very reliable. The devices have demonstrated their capability to incinerate oil and oiled debris from both accidental spills and operational

accumulation. The four incinerators are: The Portable Incinerator, the Reciprocating Kiln, the Saacke Waste Oil Burner, and the Technical Offshore Petroleum Service (T.O.P.S.) Burner.

This paper describes the operational feasibility and effectiveness of the four incinerators for a non oil spill use. Namely, the disposal of oil based muds. As each incinerator was originally developed to burn a particular medium and employs a different burn method, it was not an objective of the study to rate the incinerators against each other. More so it was an objective to analyse the burning characteristics of the muds and then possibly recommend a particular incinerator to do the job.

OIL BASED DRILLING MUDS

General

Oil based or invert emulsion drilling muds, because of their chemical composition, offer many advantages over water based muds. Both the diesel oil and mineral oil (for environmentally sensitive areas) muds offer excellent flow, filtration and oil wetting characteristics which are easily adaptable to various pressure, temperature and wellbore conditions. In addition, these muds are stable in the presence of high electrolyte concentrations, soluble gases and high temperatures.

These drilling muds are composed of an oil phase, brine phase and specialty additives. The majority of systems are composed of oil/brine ratios of either 70/30, 80/20, or 90/10. Each of these three groups serves important functions in the preparation of a stable invert emulsion (water-in-oil) and in the maintenance of required drilling fluid properties. The additives required include emulsifiers, filtration control additives, lime, organophilic clays and sometimes a weighting agent.

Drilling Mud Disposal Techniques

Muds from land wells are disposed of by various methods depending on the type of fluid and well location. Once the solids (cuttings, bentonite, etc.) are removed, waste water based muds are disposed of by either deep well injection or surface release.

Oil based fluids are either reused in the active mud system for other wells or must be treated as a waste oil and disposed of accordingly.

Waste drilling muds from offshore wells are handled as follows: As previously mentioned, about 90% of the constituent weight of additives in water based drilling muds is made up of barite, bentonite, lignite and lignosulphonate; all naturally occurring materials. There are a number of special fluids for specialized applications but generally fewer than a dozen products are required to control drilling fluid properties. All chemicals used in the drilling of offshore wells are screened and approved for use by the Federal Government. Information on the quantities of all mud components are reported to the drilling authorities.

Quantities of water based muds are wasted from the system on a daily basis due to volumetric excesses caused by the addition of chemicals and water. The total amount of drilling mud that will be discharged during the course of drilling a well will vary depending on the nature of the rocks being drilled, the complexity and cost of the fluid and time. In the case of a conventional drilling fluid, approximately 1,500 cubic metres will be

discharged in the course of drilling a 4,000 metre well (Ref. 2).

Where oil based muds are used offshore, essentially no drilling fluids are discharged. They must be separated and returned to the mud supplier, a warehouse base for longterm storage or if practical, reused in future drilling programs.

TEST METHODS

Test Muds

To make the incineration tests as authentic as possible, it was decided to use the mineral based mud that was used at the Esso Nipterk DMO-75 well. This used mud was delivered to Dome's Tuk base along with "clean" versions of both a low toxicity mineral base and a diesel base. The latter muds were produced by Technifluids in Calgary.

Test Method

The nature of this project dictated that test procedures would be finalized during the execution of the project. Timetables had to be changed frequently to accommodate equipment availability, manpower schedules and weather.

The used mineral base mud from the Esso Nipterk well had been previously centrifuged at the rig site to remove drill cuttings. The fresh muds were tested as received from Technifluids.

A test sample of each mud was presented to each of the four incinerators. Burn rates, handling procedures, visual emissions were documented and residue samples were taken for each of the tests.

The residue samples were analysed for percentage of total carbon and percentage of extractable hydrocarbon. Although the lab results from the two tests complement each other, percentage total carbon is perhaps the best indicator for burn efficiency. As it measures the total carbon content in the residue, it is directly related to the temperature of combustion. Extractable hydrocarbon indicates the extent of hydrocarbon breakdown of the primary petroleum hydrocarbons. As a baseline, raw samples of the three muds were analysed for total carbon, extractable hydrocarbon and characterization of extractable hydrocarbons.

PORTABLE INCINERATOR

Equipment Description

This incinerator was developed for Dome/Canmar in 1982 for the disposal of oil spill debris such as oiled driftwood and sorbent materials (Ref. 1). Its main design feature is the use of blower supplied combustion air to cool the walls of the firebox, thus eliminating the need for a heavy refractory lining. This unique feature allows for an efficient high rate incinerator which is transportable by helicopter to remote cleanup sites (Figure 1).

The incinerator has the capability to burn up to 1 tonne/hr. of oiled wastes. The burn is relatively smoke free and leaves a minimum of residue. Extensive testing and use in actual spill cleanups have proven its ability to incinerate a wide variety of oiled materials.



Figure 1: Air Portable Incinerator

Test Procedures

The original test concept was to feed the mud via a simple pumping device directly into the incinerator, and then use the reciprocating kiln to further reduce the oil content of the solids. It was assumed that the incinerator would not remove all of the oil from the mud and that additional processing in the kiln would be necessary. This assumption proved correct.

The portable incinerator was not designed to burn fluids. The unit was tilted to prevent leakage at the door and only small quantities of mud (.20 bbl) could be introduced at a time. In total, only one barrel of each mud was burned.

Once the mud was present in the incinerator, it was ignited using an oil spill igniter (Ref. 4). (Incidentally, the success rate of the igniters was 90%). Ignition rate of the mud surface was very slow - up to 10 minutes. The blower unit was not turned on until the entire surface area of the mud had ignited. When the blower was on at full throttle, the mud burned very hot with little visible air emissions. The incinerator's end became very red requiring a lowering of the air supply which reduced

the intensity of combustion. When this was done, air emissions increased noticeably increased.

During a burn disposal of oil based muds by Pan Arctic at Loughheed Island in 1984 a residue crust formed on the surface of the mud. During these tests, a surface crust also formed, preventing ignition of any underlying fluids. When this occurred, the crust and fluid were mixed with a 3 metre long board. If any flame was remaining, it spread to the exposed fluid and there was a dramatic increase in the flame intensity. This was a potential safety hazard to the operator. The residue (crust and fluid) was occasionally mixed until any remaining mud would not ignite. One barrel of mud produced one third barrel of residue. The residue from each of the three muds was retained for further burn tests in the reciprocating kiln.



Figure 2: Mud burn in Portable incinerator

Results

The portable incinerator was able to promote combustion of oil based drilling muds (Figure 2). However, the air flow was not strong enough to

prevent the formation of a surface crust before all the mud had been burnt. The ignition and burn rates did not vary significantly for any of the three muds.

The resulting residue included both liquid (unburnt mud) and solid (surface crust). Before the residue would be acceptable for disposal, it would require further processing. The laboratory analyses results (Table 3) are for samples that included both the liquid and solid residue. The incinerator produced only a 54% reduction in the total carbon content and a 63% reduction in the extractable hydrocarbon.

The incinerator was able to produce a smokeless burn when the air blower was on, however its inability to handle liquids makes for a labour intensive process for the operator and for a low throughput (36 bbls/day, for continuous operation).

Conclusions

The portable incinerator is not suited for the disposal of large volumes of oil based drilling muds. Small volumes (less than ten barrels) could be disposed during the incineration of other debris. However, the resulting residue from incomplete combustion, along with the required labour makes this incinerator's use impracticable for larger volumes.

RECIPROCATING KILN

Equipment Description

This device was designed to clean oiled sand and beach material by incineration (Ref. 5).

The kiln is basically a long cylinder into which oiled sand is fed. A housing holds the cylinder in a horizontal position, sloping slightly down towards the output end. A drive mechanism rocks the cylinder back and forth causing the sand to move towards the output end (Figure 3). While doing so, a fire under the cylinder heats the sand and burns off the oil. Rates of up to 1 tonne/hr of oiled sand have been processed in this manner during recent field tests.

Test Procedures

The prime purpose of this test was to analyse the kiln's ability to burn the incinerator residue for the three muds. Burn rates between the three muds should not be compared because the feed rates could not be accurately controlled.

Once the kiln reached the operating temperature, the mud residue was shovelled in. Complete ignition of the mud was slow and took a number of revolutions (15 cycles/minute). Once completely ignited, the burn maintained itself until all the oil in the residue was burned. Following a complete burn through the combustion chamber, a fine particulate solid was deposited at the output end (Figure 4).

While the kiln is better suited to the incineration of relatively solid materials, one run was made with straight drilling mud. The ignition

was immediate, however the burn rate was not rapid enough to provide a complete burn before the fluid reached the disposal end of the kiln. As a result, a rapid uncontrolled burn resulted with the flaming liquid pouring out onto the ground. Heavy black emissions were also present.

Results

The reciprocating kiln proved to be very effective for cleaning the mud residues as supplied from the incinerator. In combination with the incinerator, the total carbon content was reduced by 89% and the extractable hydrocarbons by 96% (Table 1). The kiln is also able to provide ample agitation to prevent the formation of crusts on the mud. Again, ignition and burn rates were comparable for all three muds. However, the operation would be very labour intensive with two men on continuous duty. The kiln is unable to practically process straight muds (liquid). The liquid's retention time within the kiln is not long enough to provide complete combustion.

Conclusions

In conjunction with the portable incinerator, the kiln is an option for the cleaning and disposal of small volumes of oil based drilling muds.

Potential does exist for the cleaning of drill cuttings, however modifications would be required to increase the throughput rates.

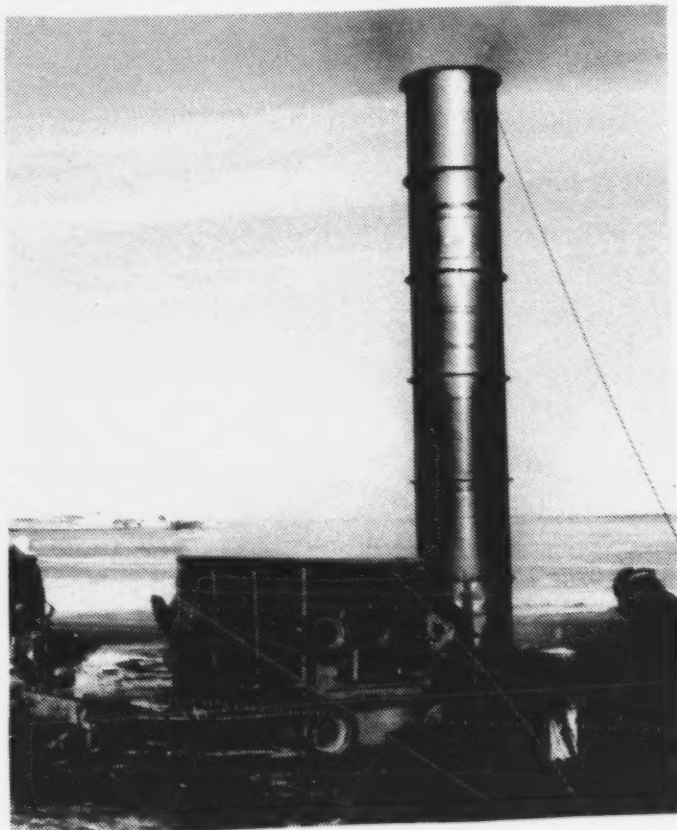


Figure 3: The Reciprocating Kiln

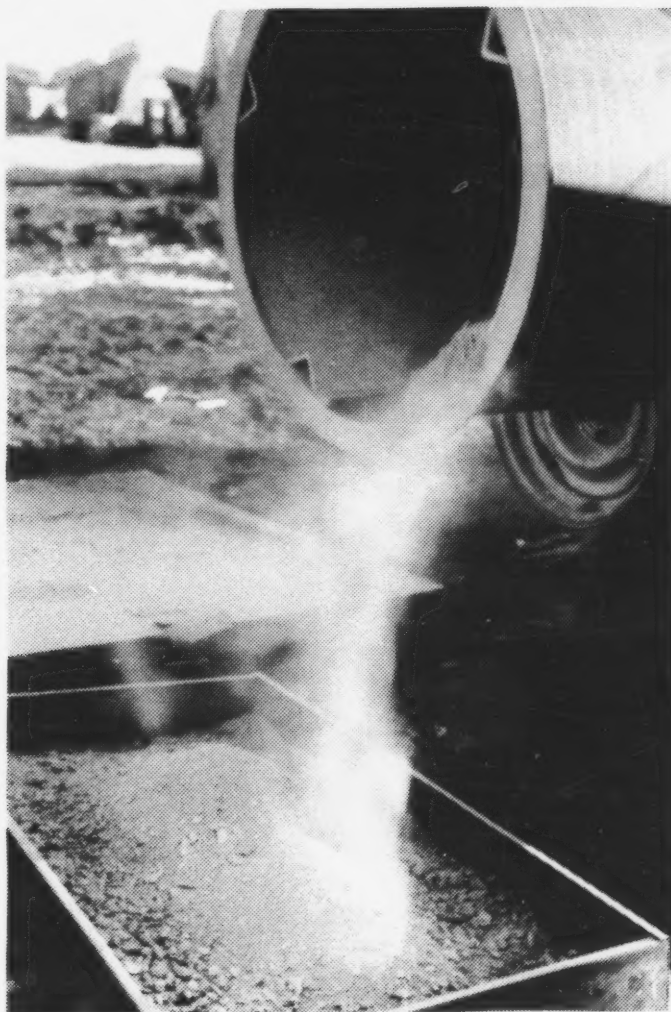


Figure 4: Residue at output end of Kiln

SAACKE WASTE OIL BURNER

Equipment Description

This burner was developed as a spill response incinerator for Dome/Canmar in 1979, and has also been used for the disposal of waste oils from the Beaufort drilling and marine operations (Ref. 3). The waste oils include used lubricants and hydraulic fluids, water contaminated fuels, tank washings and oil recovered from oil spills (Figure 5).

The burner is fully self-contained and transportable by helicopter. It is capable of burning 40 m³/day (250 bbls/day) of oil, and can continuously burn oil/water mixtures containing 60% water. The burn is smoke free with no appreciable fallout. Non-combustible products (e.g. oil tank washings, oil/mud mixtures) have been handled by pre-mixing them with other waste oils and then burning the mixture.

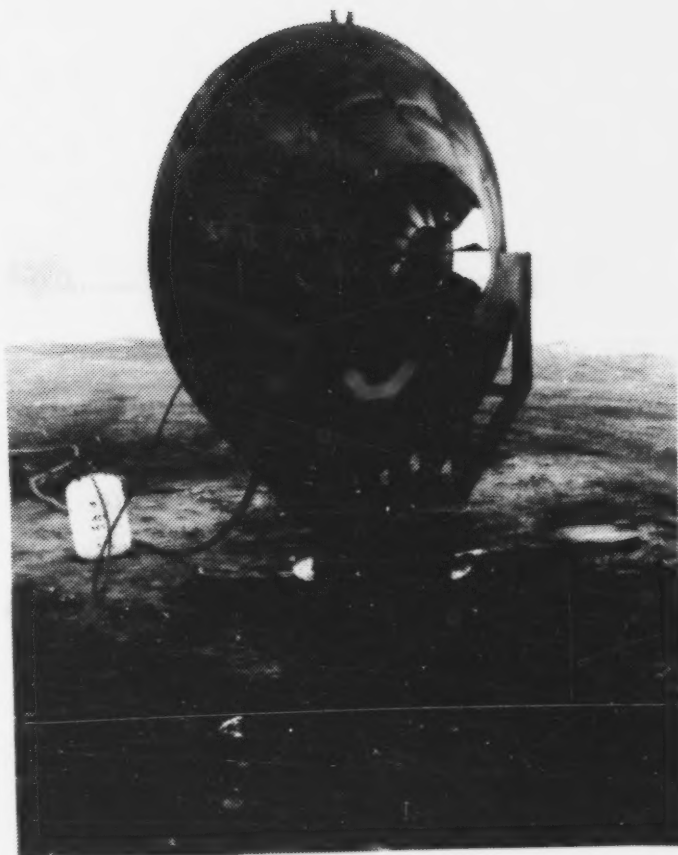


Figure 5: The Saacke Waste Oil Burner

Test Procedures

The individual muds were pumped into a holding tank from which they were pumped through a pre-heating chamber and 30 m. lines to the burner head. This was the first time that fluids with a high solids content were fed through the SAACKE system. As expected, the solids clogged the filter

system and transfer lines. It also caked the rotary cup at the burner head. Considerable noise and vibration were experienced. In spite of this uncut muds could be burned but because of the solid's effect, the initial burns were discontinued.

To reduce the solids content, the muds were diluted from 20 to 50% with discarded JP-4 jet fuel. This was done in the holding tank with subsequent circulation. The burn rates, shown in Table 1 are net for mud only. The Saacke burn rates for the three muds cannot be properly compared as considerable adjustments had to be continually made to the Saacke due to the solids content. However, the average rate does provide a basis for comparison with the other burner units.

Visible air emissions were light and white in colour during all tests. The emissions were thought to be barite however it was difficult to obtain residue samples. Visible emissions were negligible during the 50% jet fuel dilution of the fresh diesel base mud. Later it was evident that the jet fuel had caused a large amount of solids to settle out in the holding tank. This reduced the solid content of the mud that was pumped to the burner head. However, solids were still found caked onto the burner head.

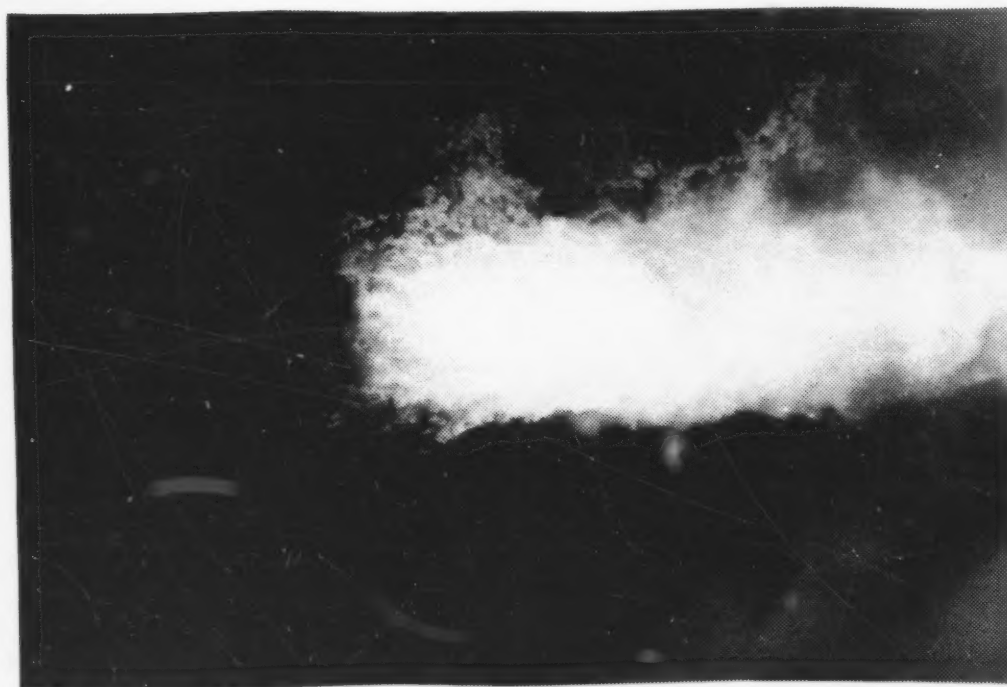


Figure 6: Saacke mud burn.

Flame temperatures were also taken during the Saacke tests using a hand held infrared monitor. The mud left the burner nozzle at a preheated temperature of 55°C. Flame temperature was 830°C whereas the burner head shroud measured 300°C. A total of 28 barrels of mud were burned with the Saacke (Figure 6).

Results

These trials indicate that the Saacke burner is capable of burning all three muds with equal efficiency. However, it would be impossible to process large volumes of these muds without modifying either the burner or the mud (i.e. through cutting with some other fuel) to reduce the effect of the solids content. In these trials, this was accomplished by adding the JP-4 to the mud. For operational disposals, it may be possible to combine drilling mud with other slops slated for disposal. Conversely, it may be possible to modify the filtering system of the Saacke in order to accommodate a high solid load.

Once burning, the Saacke effectively reduced the oil content of the mud (Table 1) and left only a fine white powder that escaped in the smoke produced by the burns. Residue fallout was negligible in the immediate area and downwind of the burner. Samples had to be scraped from a pan placed under the flame and from the face of the Saacke.

In summary, the Saacke burner shows definite potential for the disposal of oil based drilling muds. However considerable work on the design of the system, or care in coordinating mud disposal with other waste oil disposal would be required before this device could be considered to be an operational tool for this purpose.

Conclusions

The Saacke burner proved to be a potential device for incinerating oil based drilling muds. However, the present system design does not efficiently handle the solids content of the muds without the possibility of mechanical and structural damage to the burner.

It is possible to process (i.e. burn) these muds if they are combined with a fluid that will reduce the solids content. It also may be possible to devise a method to introduce the muds at the burner head while disposing of other slops oil.

As residue fallout was negligible in the immediate area downwind from the Saacke, samples could not always be collected. Visible emissions appeared to be primarily due to the solids content.

TECHNICAL OFFSHORE PETROLEUM SERVICES BURNER (T.O.P.S.)

Equipment Description

This device is currently used offshore during well testing to dispose of produced hydrocarbons. A unit has also been installed on the Beaufort Sea Oil Spill Cooperative's Response Barge to dispose of large volumes of oil that might be collected in a marine clean up operation. It can burn up to 80 tonnes/hr. (12,0000 bbls/day) of crude oil.

The burner head utilizes specially designed atomizing nozzles and pressurized air to atomize the oil into a fine mist. The mist is ignited by propane fueled igniters. A water spray into the flame reduces the smoke to a minimal amount (Figure 7).

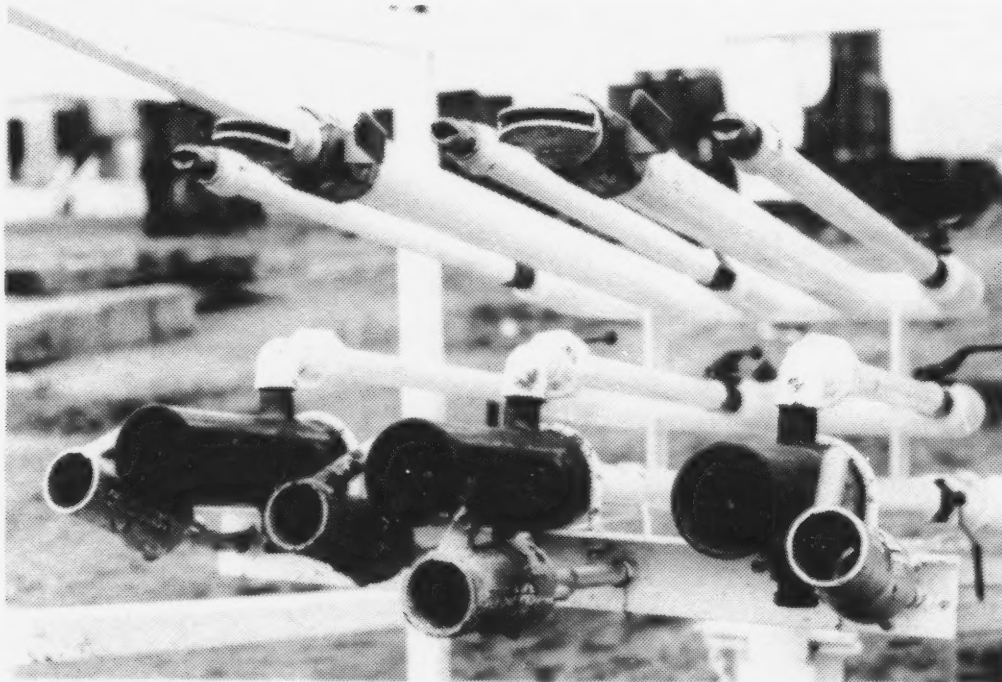


Figure 7: T.O.P.S. Burner Head

Test Procedures

The T.O.P.S. unit was not accompanied by completely compatible support equipment as it would have been if rig mounted. Although the support equipment was the best available at the Tuktoyuktuk site it did fall short of adequately fulfilling the T.O.P.S. burner's requirements. Problems were experienced with the electrical and water supplies, and pump pressures.

The small quantities of mud along with the available support equipment restricted the use of the burner heads to one third of their capacity.

The water spray was found to restrict the combustion of the mud thereby causing fallout and high visible emissions. Without the water

spray, no samples were found in the fallout trays and the visible emissions were considerably reduced (Figure 8).



Figure 8: T.O.P.S. mud burn

Results

In spite of the equipment difficulties mentioned above, the T.O.P.S. burner proved to be the most successful of the four burners tested for the incineration of oil based muds. It is the view of the authors of this paper that with minor alterations, this unit could be used operationally to dispose of large mud volumes. Even with the limitations imposed by the use of undersized pumps and power supplies, the T.O.P.S. burner was capable of burning these muds at an average rate of 331 bbl/day (Table 6). If the proper support equipment were available and properly adjusted, then complete destruction of larger mud volumes would be possible.

In addition to the high burn rates, the amount of smoke produced during these burns was minimal. These air emissions were not sampled, but probably consisted of unburned hydrocarbons and airborne solids from the

mud. Samples of the residue fallout indicated that the incineration process had removed 100% of the Total Carbon content. If a burn were conducted on an offshore rig, the fallout from the burner could enter the ocean without concern for hydrocarbon pollution.

In summary, this burner showed the most promise for oil based mud disposal and with minor modification, could be used on an operational level.

Conclusions

The T.O.P.S. burner was capable of burning all three muds and of efficiently handling the high solids content of these fluids. Ignition was immediate with complete combustion of the oil in the muds. The solids residue was airborne and 100% free of hydrocarbon residue.

The burner's rig location during well testing makes it the best immediate alternative for the incineration of oil based mud. Two men are required to safely operate the T.O.P.S. burner. However, if rig mounted, the expense, time and manpower required to transfer the mud to shorebase would be eliminated.

TABLE I
Comparison of the Four Methods for
the Incineration of Oil Based Drilling Muds

	Average Burn Rate Bbl/day	Average % Reduction Total Carbon	Average % Reduction Extractable Residue Hydrocarbon		Visible Air Emissions	Labour Intensity	Pretreatment Required of Muds	Practicality Offshore Use	Usefulness of Device Mud Burning	Overall Ranking
Incinerator	36	54	63	Oily Crust	Low (dark)	High	None	Very Low	Very Low	poor
Kiln	24	89	96	Dry Clay	Low (Dark)	High	- large % of liquid removed	Very Low	Very Low	poor
SAACKE	166	99	100	Light Airborne Dust (Clay)	Moderate to Heavy (white)	Moderate	- cuttings removed - diluted to reduce solid concentration	Moderate	Moderate	feasible
T.O.P.S.	331	100	100	Light Airborne Dust (Clay) *Less than Saacke	Moderate (white to dark)	Low	None	High	High	excellent

STUDY CONCLUSIONS

1. For each of the incinerators, it was found that all three muds could be burned with equal efficiency. The fact that a mud was fresh or used, mineral based or diesel based had no effect on its ability to burn.
2. To burn effectively, muds have to be in a thin film or aerosol. In the tests where this was not incorporated an aerosol burn, a surface crust formed which extinguished the burn.
3. The T.O.P.S. burner proved to be the most effective incinerator for oil based mud disposal. The burner can be used operationally at a rig site thereby eliminating the expense, time and manpower required to transfer the mud to shorebase. The use of the Saacke burner for mud incineration is not feasible due to the muds' solid content. Only with significant modifications should the Saacke be considered. The low throughput and labour requirements for the portable incinerator and reciprocating kiln combination limits their operational use.
4. The authors believe that the airborne emissions from the Saacke and T.O.P.S. burners contain negligible hydrocarbons which would allow for an acceptable release into the environment. It is also felt that the residue from the incinerator/kiln burns would be acceptable for disposal.
5. It is possible to burn the muds in all four devices with minimal visual air emissions. However, it is suggested that there is a provision for air sampling in any future mud burning trials.

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ALASKA CLEAN SEAS SURVEY AND ANALYSIS OF AIR-DEPLOYABLE IGNITERS

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ABSTRACT

An assessment has been completed of the physical and operational characteristics of several existing and potential aerial ignition systems. This survey and analysis has been conducted to help identify and construct some alternate ignition concept(s) that might prove more efficient and less costly than those currently available. Ignition systems selected for examination during this first phase of the igniter development program include the EPS or "PYROID" igniter (made by Astra Pyrotechnics Ltd.); the Dome Igniter (made by Energetex Engineering); laser igniters (tested and evaluated by Arctec Canada, Ltd/Physical Sciences Inc. for EPS, Environment Canada); the Helitorch igniter (made by Simplex Manufacturing Co.); and the Premo Aerial Ignition Device (made by Premo Plastics Engineering Ltd). Presented in this paper is a summary of the physical and operational characteristics of each ignition system and a comparative analysis of at least 30 important assessment criteria by which any igniter could be evaluated.

BACKGROUND AND OBJECTIVES

This paper contains a summary of a much more extensive report prepared by Spiltec and administered by Shell Western E&P Inc. for Alaska Clean Seas (ACS), an oil-industry-sponsored oil spill response organization based in Anchorage, Alaska. The original report, Survey and Analysis of Air Deployable Igniters (Spiltec, 1986), presents the results of one of several R&D efforts sponsored by ACS during 1985.

It is well recognized that in-situ burning is one of several oil spill control measures that may be selected under certain circumstances to reduce the overall potential for environmental impact. The burning of oil in place may be a viable response option, particularly when it is unsafe or impractical to use physical removal techniques effectively. The most important, and often very difficult, step in conducting an in-situ burn is the safe and efficient ignition of the spilled oil. And when the oil is floating on water, the ignition process must usually be initiated from the air. This report contains the results of a one-year survey and analysis of existing and potential aerial ignition systems for initiating the combustion of floating oil slicks in arctic or subarctic conditions. The following ignition systems were selected for examination during this first phase of an ongoing igniter development program:

- o EPS Igniter -- Initially designed by the Canadian Defence Research Establishment, Valcartier (DREV), developed and tested by the Environmental Protection Service (EPS) as part of the Arctic

Marine Oilspill Program (AMOP), and subsequently manufactured by ABA Chemical Ltd. (now Astra Pyrotechnics Ltd.), in Guelph, Ontario. The igniter is also known as the "PYROID" igniter, which is currently manufactured and marketed by Astra Pyrotechnics Ltd.

- o Dome Igniter -- Developed for Dome Petroleum Ltd, Calgary, Alberta, by Energetex Engineering, Waterloo, Ontario. The Dome igniter is currently manufactured by Energetex Engineering.
- o Laser Igniter -- Tested and evaluated by Physical Sciences Inc., Andover, Massachusetts, under contract to Arctec Canada, Ltd., for the Environmental Protection Service, Environment Canada.
- o Helitorch Ignition System -- A proven aerial ignition system for igniting forest slash, backfires on forest and range fires, and for field burning. Having been used extensively throughout the U.S., Canada and other countries, the Helitorch is currently available through the U.S. Forest Service, the Canadian Forestry Service and various suppliers (e.g., Simplex Manufacturing Co., Portland, Oregon).
- o Premo Aerial Ignition Device. Another commonly used ignition system for controlled burning on land. The Premo Aerial Ignition Device (AID), sometimes referred to as the "ping-pong ball" igniter, is currently manufactured and marketed by Premo Plastics Engineering Ltd., Victoria, B.C.

Any ignition system that involves an object (or burning agent) dropped onto an oil slick must produce a minimum of slick disturbance while delivering sufficient heat to volatilize the oil and then ignite the resulting vapors. Whatever the ignition system is, it must have a reasonable degree of success under a broad range of wind and sea conditions on slicks that would normally be considered combustible.

Research in the United States and Canada has repeatedly confirmed the feasibility of burning both fresh and weathered oil slicks on water (Buist et al., 1981; Industry Task Group, 1983). It is well known that combustion can be sustained as long as the heat feedback from the flames is enough to compensate for the heat loss to the water beneath the slick and provide the heat required to produce sufficient vapors for the fire. As soon as the burning layer of oil approaches a thickness of typically 1 to 3 mm (depending primarily on the type and age of the oil), excessive heat loss to the water will cause the fire to go out.

Any ignition system is therefore dependent upon the availability of oil sufficiently thick to support its sustained burning down to approximately 1 to 3 mm (or about 1/10 in.). Even under arctic conditions, oil being burned in-situ will normally have to be contained by natural barriers, wind-herded by natural or artificial means, and/or prevented from spreading by fire-resistant booms. Without containment, burn efficiencies of 50% to 60% or less may result even when the initial oil layer is in excess of the minimum burn thickness (Industry Task Group, 1983). With containment, however, 98% or more of the oil may be eliminated.

A comparison of the existing and potential oil slick ignition devices listed above has been attempted in this study in spite of the very different operational modes of the five systems selected. The objective of making this comparison is not to provide a ranking of the igniters, but to provide a factual basis from which desirable and undesirable igniter characteristics can be identified. By comparing the five ignition concepts within a sufficiently broad range of assessment criteria, it is hoped that the strong and weak points for each system will help reveal the "ideal" characteristics for a new and improved igniter.

IGNITER PERFORMANCE CRITERIA

The development of appropriate igniter performance criteria must reflect the kinds of oil spill "targets" on which the igniters are intended for use. Such targets might be single large spills that are relatively thick and continuous (e.g., at a major tanker accident), or they might be a large number of relatively small oil slicks spread over an extensive region. The latter case might result from the uncontrolled movement of a continuous oil spill into a moving broken ice field or beneath a moving solid ice cover over an extended period of time. It is this scenario involving a subsea blowout in the Beaufort Sea that has been of significant concern during several Canadian investigations into the feasibility of in-situ burning (Ross, 1981; Meikle, 1981). As the ice begins to melt in the spring, oil trapped in the ice would migrate to the surface of the ice through brine channels and accumulate on melt pools on the ice surface.

The potential for a major spill involving such widespread pools of oil is highly unlikely; however, if such a spill event occurred in the Arctic, it could require the release of many 100's to 1,000's of individual igniters. For this reason, some of the most important considerations for an effective igniter will involve the cost to manufacture and deploy the units, and the speed and accuracy with which they can be placed in the oil. Based on previous experimental tests with oil exposed during early breakup, it is quite reasonable to assume that the majority of oil available for burning in melt pools would exist in irregular pools typically 1 to 10 m across on the average. Depending upon many conditions at the time of the spill (e.g., oil flow rate, amount of gas, ice condition and rate of movement, etc.), the spacing between such exposed oil pools could vary from only a meter to a hundred meters or more.

Other areas of consideration for a practical and efficient aerial ignition system must include safety, storage requirements, shelf life, durability, simplicity of design and use, availability (and construction time), and most of all, reliability. An aerial igniter must consistently survive the fall and impact of a release from at least 10 to 15 m altitude, land with minimal disturbance of the surface slick, provide sufficient heat to volatilize the oil nearby, and burn long enough and hot enough to create a self-sustaining flame over the oil surrounding the igniter. Ideally, the heat then generated from the burning oil at the igniter should be sufficient to promote flame spread over the entire slick.

The type of flame produced during the initial volatilization and vapor-ignition phase must be "soft." That is, the flames must not be blown at the oil/water surface causing the oil to move away from the igniter. A

gentle, though very hot heat source must be oriented with the surrounding oil to minimize any disturbance of the slick while maximizing the transfer of heat to the oil. If possible, the ignition system should provide some means of isolating or protecting a portion of the oil from the effects of strong winds that might otherwise separate the igniter from the oil being heated and/or blow the initial flames completely out.

The shape of an igniter is important as it relates to the accuracy of the igniter's trajectory during freefall and as it influences the igniter's ability to stay on target. Should the igniter be too light and have a large cross-section, it may drift or be blown away too easily from its intended oil pool. The shape of the igniter must also be considered in minimizing any tendencies for the igniter to bounce or skip upon impact with a solid or shallow-water substrate. Upon impact, the igniter should suffer little or no damage, it should remain at or very close to its point of impact, and it should be able to function effectively independent of its orientation.

An important safety requirement for an aerial igniter is the need to have its starter (i.e., the "igniter" of the igniter) complete its function outside and away from the aerial platform being used. There should be no open flame or sparks produced within the aircraft. The starter mechanism should be sufficiently protected or isolated from the igniter to ensure that no igniter could possibly be activated prematurely. All handling of the igniter and its starter should also be simple with instructions clearly marked on the unit so that relatively unskilled personnel could operate it safely.

In all cases (i.e., whether ignited prior to or after impact), the starter should be capable of activating the igniter even if the starter has become temporarily submerged or heavily doused with water. Once the igniter is fully activated, any sea state that might put the igniter out would also very likely prevent the formation of a combustible oil layer.

Other than the above economic and operational considerations, an acceptable aerial ignition system should also present little, if any, environmental concern. The igniter itself should be consumed in the resulting fire, or any parts remaining after a burn should cause an insignificant impact on the environment even when very large numbers are used. In addition, any igniter that fails to ignite should be safe to handle during its recovery. This inherent safety feature (following a misfire) could be related to the igniter's failsafe design or its subsequent decomposition during exposure to the environment.

EXISTING OIL SPILL IGNITION SYSTEMS

The state-of-the-art in aerial igniter deployment concepts has been achieved in large part from the efforts of government, oil industry, and contractor support groups located in Canada (Energetex Engineering, 1978; Dickens, 1979; Meikle, 1981; Energetex Engineering, 1982; Twardawa and Couture, 1983). In this development effort, numerous ignition systems were considered including sodium-coated metal cylinders, sodium with gasoline, solid fuel and solid propellants, Thermite, hypergols, and various conventional flares. In addition, several starter concepts were also evaluated including chemical, electrical, fuse wire, mechanical, and radio-activated. The advantages and disadvantages of many of these concepts

are summarized by Energetex Engineering (1978). From these efforts, the EPS and Dome igniters surfaced during the early 1980's as representative of what could be developed using the best available technology.

Environmental Protection Service (EPS) Igniter

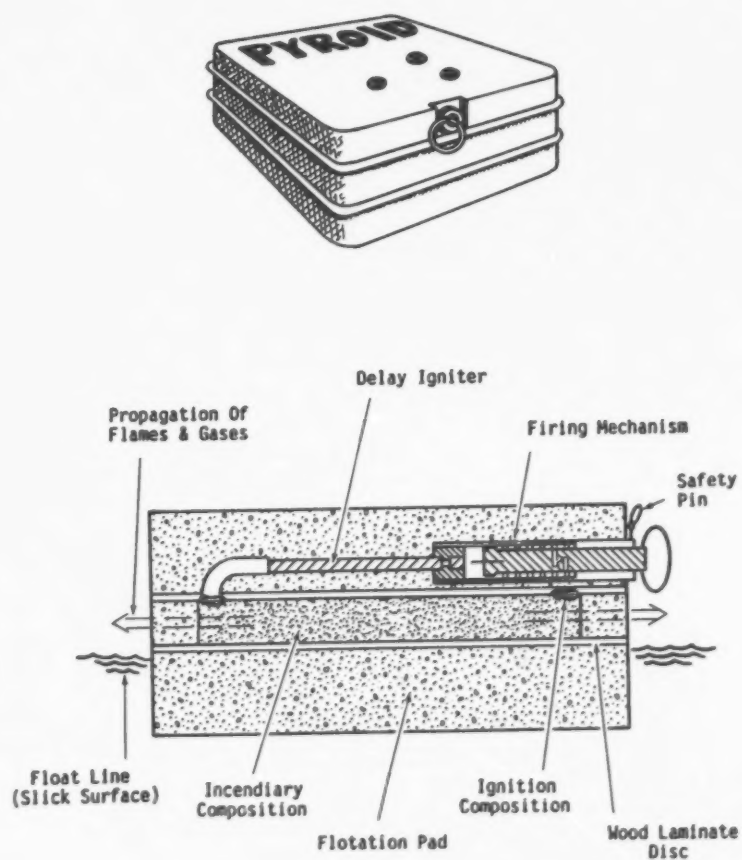
The EPS igniter is an air-deployable pyrotechnic device developed by the Environmental Protection Service, Environment Canada, in cooperation with Defence Research Establishment, Valcartier (DREV) and the Arctic Marine Oilspill Program (AMOP). The igniter (Figure 1) is approximately 25 cm (10 inches) square and 12.5 cm (5 inches) high and weighs nearly 2 kg (4 1/2 lb). The unit consists of a pyrotechnic device sandwiched between two layers of flotation and activated by a self-contained firing mechanism. It is intended to be a hand-thrown device for the ignition of contained spills where in-situ combustion has been approved and can be done without threat to personnel, equipment, and the environment.

Initially manufactured by ABA Chemical Ltd. (now Astra Pyrotechnics Ltd.), the EPS igniter has been marketed as the "PYROID" igniter. It is simple in design and operation, being activated by pulling on a firing clip which in turn strikes a primer cap. A 25-second delay column then provides sufficient time to toss the igniter and let it settle within the target oil slick. A specially formulated ring of fast-burning ignition composition is then ignited, and this in turn ignites the primary incendiary composition. The incendiary composition is basically a proven rocket motor propellant consisting of typically 40% to 70% ammonium perchlorate, 10% to 30% metal fuel (magnesium or aluminum), 14% to 22% binder, and small amounts of other ingredients to aid in the casting and curing processes. These materials have an estimated shelf life of about 5 years.

The firing mechanism and the incendiary materials are sandwiched between two polystyrene pads to provide both buoyancy and protection for the device on impact. All components except the firing mechanism are combustible, so that very little debris is left in the environment after a burn. These components have also been designed so that the igniter experiences a minimum of roll if dropped onto a hard surface or shallow water, so that the igniter can float in as little as 5 cm (2 inches) of water/oil and so that the flame released will be oriented properly with the oil regardless of which side of the igniter is up. The EPS igniter has been designed to produce a ring of fire with temperatures approaching 2,300°C (4,172°F) immediately adjacent to the perimeter of the igniter. This intense flame has a typical duration of about 2 minutes.

Dome Igniter

The Dome igniter is a lightweight, air-deployable pyrotechnic device developed by Dome Petroleum Ltd., Calgary, Alberta, in cooperation with Energetex Engineering, Waterloo, Ontario. The igniter (Figure 2) measures approximately 30 by 18 by 11 cm and weighs approximately 1/2 kg. The unit consists of a wire-mesh fuel basket with solid propellant and gelled kerosene slabs suspended between two metal floats. Like the EPS igniter, the Dome unit is intended as a hand-thrown device for the ignition of contained spills where in-situ combustion of oil has been approved and can be done without threat to personnel, equipment, and the environment.



After: Twardawa & Couture, 1983.

FIGURE 1

ENVIRONMENTAL PROTECTION SERVICE (EPS) IGNITER, OR PYROID IGNITER, SHOWING INTERNAL FIRING MECHANISM AND PYROTECHNIC COMPONENTS

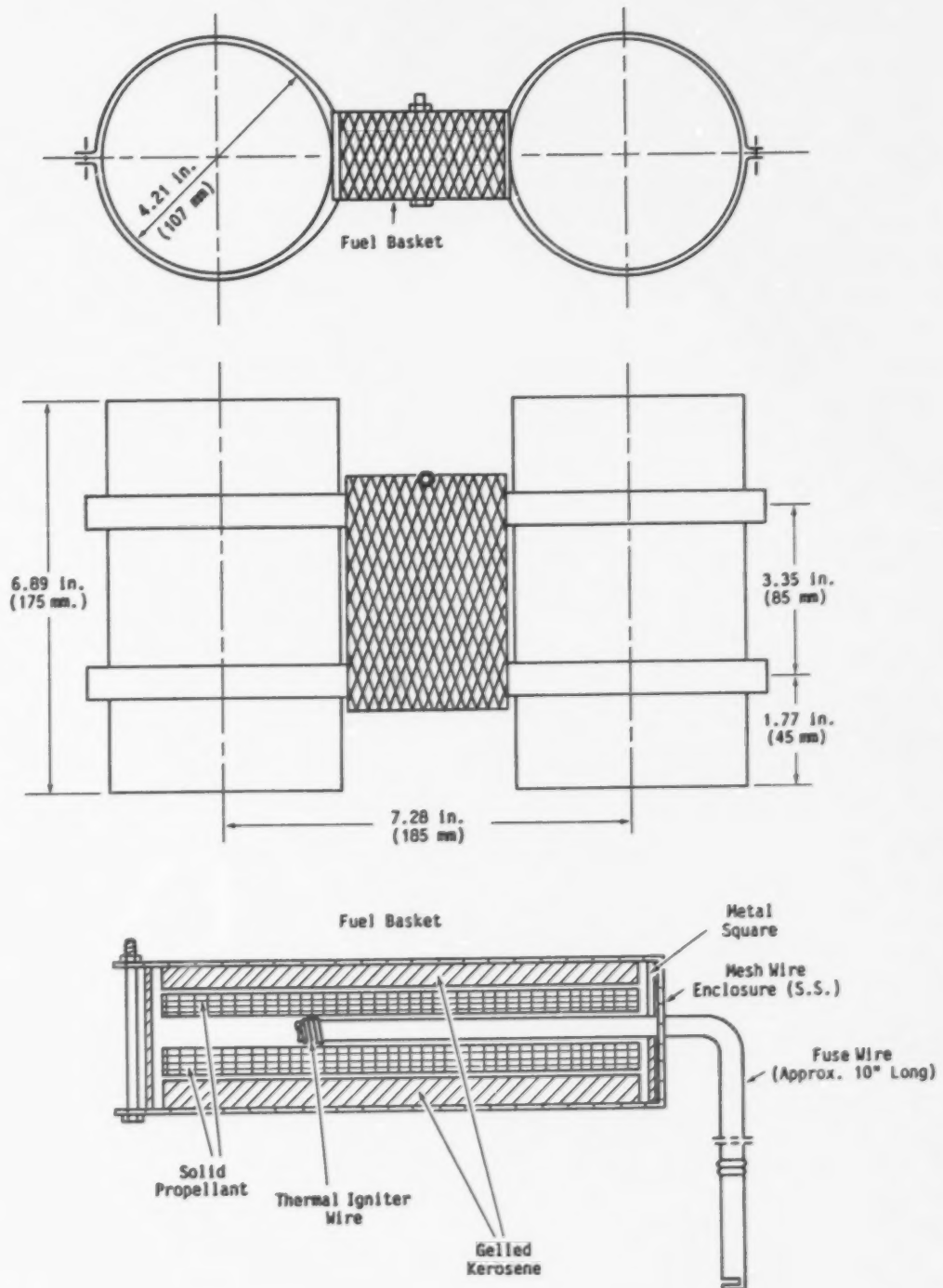


FIGURE 2 BASIC DESIGN AND INTERNAL COMPONENTS OF THE DOME PETROLEUM LTD. IGNITER

The Dome igniter is currently manufactured by Energetex Engineering and has come to be known in some regions of the U.S. and Canada as the Energetex igniter or the "tin-can" igniter. It has gone through a few design changes since it was first tested by Dome during the winter of 1979/1980. These changes have involved the igniter's mode of activation and the way in which certain components in its fuel basket are isolated from each other. In order to avoid any need for open flame during activation, the fuse wire is now started with a specially designed electric ignition system referred to as the Energetex Engineering Ignition System (EEIS). Consisting of a 12-volt, spill-proof battery with a gel electrolyte and a conveniently mounted heater element, the EEIS can provide sufficient heat to activate the igniter's fuse wire within 2 seconds of contact. Once started, the 25-cm-long fuse wire provides about 45 seconds of delay for tossing the igniter and allowing it to settle within the target oil slick.

The time-delay safety fuse then ignites a thermal igniter wire, which in turn ignites the solid propellant slabs located above and below the igniter wire. The solid propellant burns intensely for about 10 seconds with temperatures in excess of 2,000°C (3,700°F). During this initial burn, the gelled kerosene then begins to burn producing temperatures of approximately 1,200°C (2,200°F) to 1,300°C (2,400°F). The total burn time for the igniter is about 10 minutes.

Because of the very shallow draft of the igniter, the fuel basket housing the propellant and gelled kerosene is suspended above the oil layer. The oil between the floats and beneath the fuel basket is somewhat shielded from the wind, so that the warming and volatilization of the oil are enhanced. When the oil is sufficiently heated, the flames directly beneath and around the igniter soon become self-sustaining. The relatively long burn-time for the Dome igniter helps keep the slick lit if winds temporarily separate the igniter from the heaviest concentrations of oil. Upon completion of the burn, all of the metal components of the igniter remain at the surface of the water and attached to the two floats.

The lightness and irregular shape of the igniter are desirable because these characteristics give the igniter a relatively low impact velocity and a tendency to avoid rolling. The igniter has only two stable positions in which it can float, and either one keeps the igniter's flames in close proximity to and slightly above the oil.

POTENTIAL OIL SPILL IGNITION SYSTEMS

For use in igniting oil from the air, the Dome and EPS igniters described in the previous section must be released manually one at a time from a slow-moving helicopter. Depending on the number, spacing, and location of the slicks relative to the staging area; the number of aircraft available; weather conditions; etc., this method of deployment may not be the most cost-effective and timely way to ignite an extensive region of individual slicks. The concepts described in this section for igniting oil slicks are therefore presented as potential options in the continuing search for additional methods of carrying out large-scale in-situ burning operations. These methods, or variations/combinations of them, may eventually provide techniques to supplement existing mechanical devices such as the EPS and Dome igniters.

Laser Igniter

During the past few years, serious consideration has been given to the feasibility of using lasers to ignite oil spills on water. Under the sponsorship of the EPS, Environment Canada, several laboratory and controlled field tests have been conducted to establish the feasibility of igniting oil slicks with commercially available lasers. Under contract to Arctec Canada Ltd., scientists with Physical Sciences Inc. (PSI), Andover, Massachusetts, have tested various laser techniques, successfully igniting warm and cold oil slicks of varying types and degrees of weathering. This approach is considerably different than the pyrotechnic ignition devices described in the previous sections; however, the long-range objective is similarly the ignition of large numbers of remote oil slicks. Such a spill scenario could conceivably result from the disabling of a tanker or from a blowout where oil is released into a moving ice field and later surfaces as many thousands of individual pools of oil in the spring.

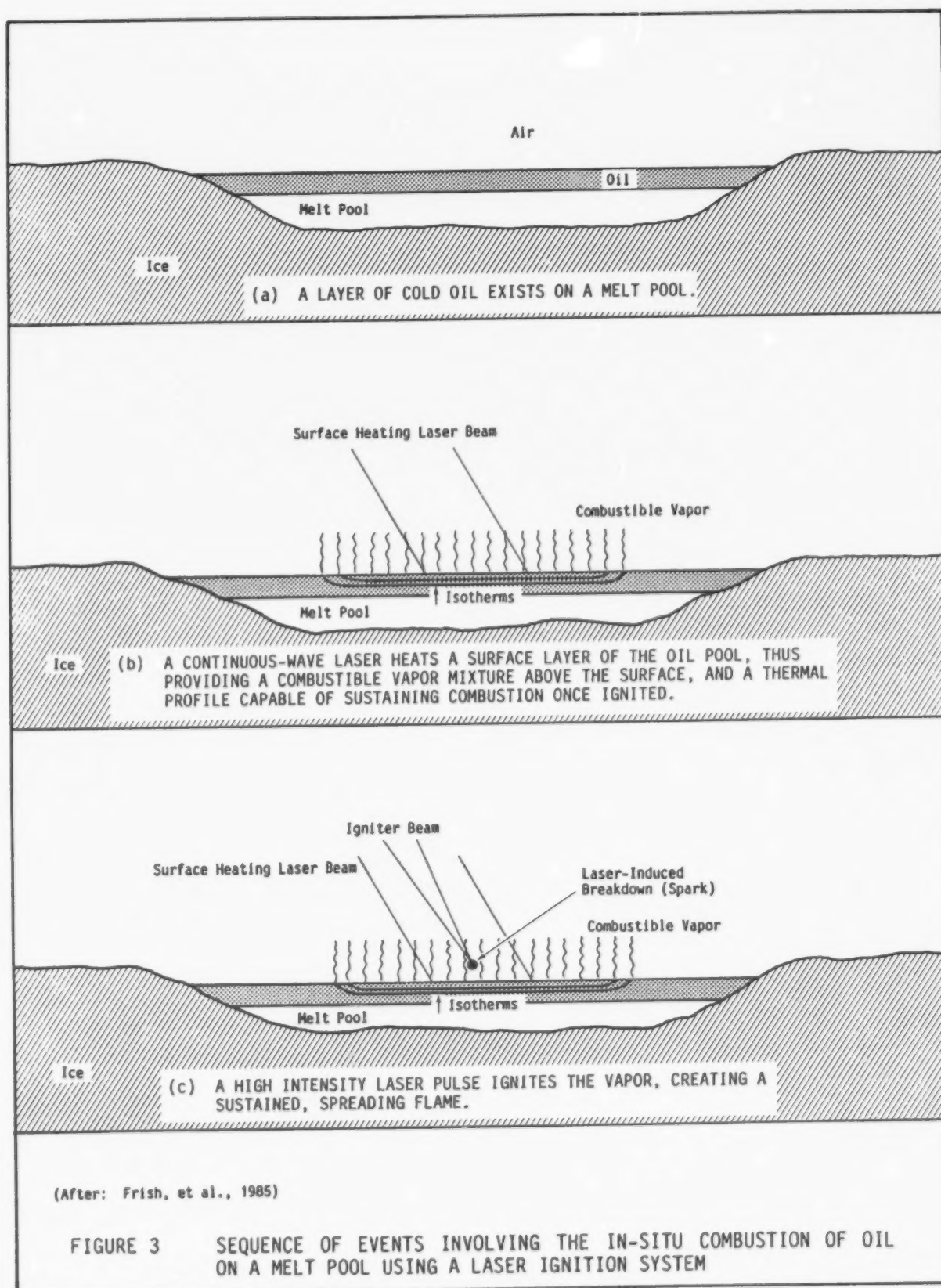
PSI representatives have been successful in using a dual-laser approach in starting fires in pooled oil. Working with laboratory conditions and with cold oil layers under simulated arctic conditions, they used a continuous-wave CO₂ laser to heat a localized area of an oil pool to create surface temperatures above the oil's fire point (Figure 3). The heating time varies with the oil type and condition, air temperature, wind conditions, etc., but is typically a few seconds to more than 30 seconds. A focused high-power pulse from a second laser is then aimed at the vapors above the heated oil layer to ignite them. These tests have been conducted to determine the preheating and ignition requirements to provide an adequate flame that will be both self-sustaining and intense enough to insure the spread of flame over the entire pool of oil.

Frish *et al.* (1985) summarizes the above heating mechanisms, specific operating characteristics of the lasers used, and the detailed results of many tests conducted thus far. For the purposes of this igniter survey, it is sufficient to note that existing laser packages have been demonstrated and proven successful in igniting cold oil layers under controlled, small-scale, static conditions. With some modifications, such laser systems should be adaptable for mounting in helicopters. Based on the experiences to date, it is clear that a considerable effort is still required to design and test helicopter-mounted optical systems for focusing the laser beams, shock-mounts to absorb unwanted vibrations, and a number of systems that will be necessary to accurately aim at and determine the range to a spill target.

Helitorch Igniter

The Helitorch is an ignition system which uses burning gelled gasoline or diesel released from a helicopter-slung unit. It is a proven aerial ignition system commonly used by the U.S. Forest Service and the Canadian Forestry Service for the burning of forest slash and for setting backfires during fire-control operations. The Helitorch has not been used to ignite waterborne oil spills; however, there is reason to believe that the same ignition concept may have some merits for the burning of oil slicks in situ.

The Helitorch is a completely self-contained unit consisting of a fuel barrel, pump, and motor assembly slung beneath a helicopter and controlled with an electrical connection from the Helitorch to a panel in the cockpit.



The fuel barrel is filled with a gelled gasoline or gasoline-and-diesel mix (basically napalm) which is pumped upon demand to a positive-control shut-off valve and ignition tip (Figure 4). The gelled mixture is ignited as it is pumped from the unit, and a highly viscous stream of burning fluid is produced. Some systems rely on electrical ignition alone, while others have been modified to incorporate an electrically activated propane flame to insure positive and continuous ignition of the fluid as it is released. As the burning fluid falls from the unit, it soon breaks up into fireballs, the size of which depends upon the viscosity of the mix and the airspeed of the helicopter.

The size of the fireballs at ground level also depends on the altitude upon release. For example, if released from a height of approximately 90 m (300 ft) at an airspeed of 96 km/hr (60 mph), a typical mixture of gelled gasoline will produce burning gel/gas particles the size of golf balls at ground level. These burning blobs will flatten out upon impact on a hard surface and burn for approximately 8 to 10 minutes. If the same material is released from a height of 45 m (150 ft) at an airspeed of 48 km/hr (30 mph), the burning particles will normally be about the size of baseballs, with a sustained burn time on the ground of 12 to 17 minutes. Because such releases are normally conducted over trees and other debris, comparable data has not been found for the results of aerial drops from much lower altitudes. Data is also needed for burn times on water.

The Helitorch ignition system is manufactured by Simplex Manufacturing Co. in Portland, Oregon, and is approved by the Federal Aviation Administration (FAR Part 137). The unit can be carried by any helicopter with a cargo hook and 28-volt power supply. The weight of the package with a full 208-liter (55-gal) drum is approximately 242 kg (534 lb). When it is operated with a fan nozzle, an effective swath width of 4½ to 9 m (15 to 30 ft) can be achieved. The manufacturer recommends a gelled fuel application rate of 14 to 28 liters/hectare (1.5 to 3 gal per acre). If flown at normal application speeds (say 48 to 96 km/hr, or 30 to 60 mph), the Helitorch can produce initial burn exposure rates in excess of 1.2 hectares per minute (3 acres per minute) while releasing the gelled fuel. At 28 liters/hectare, a 208-liter payload could require up to 18 minutes of application time per sortie.

Premo Aerial Ignition Device

The Premo Aerial Ignition Device (AID) is an ignition concept that could lend itself to the design of a new and improved air-deployable igniter for floating oil slicks. The igniter has undergone much development work by Mr. Gary Lait, Fire Research Technician with the Canadian Forestry Service, Victoria, British Columbia, and is currently manufactured by Premo Plastics Engineering Ltd., Victoria, B.C. A proven and very reliable igniter for debris burning and forest fire control, the Premo AID is a polystyrene spherical container about 3 cm (1 1/4 inches) in diameter with approximately 3 grams of potassium permanganate inside. Once the container is injected with a small volume (typically 1 cc) of glycol, an exothermic reaction is initiated resulting in the destruction of the spherical container with flames lasting about 20 to 30 seconds.

The particle size and concentration of the chemicals involved will determine the rate of the resulting chemical reaction. Experience has shown, for example, that water-glycol solutions ranging from 50% to 100% concentration of glycol will provide reliable ignition with a time delay of

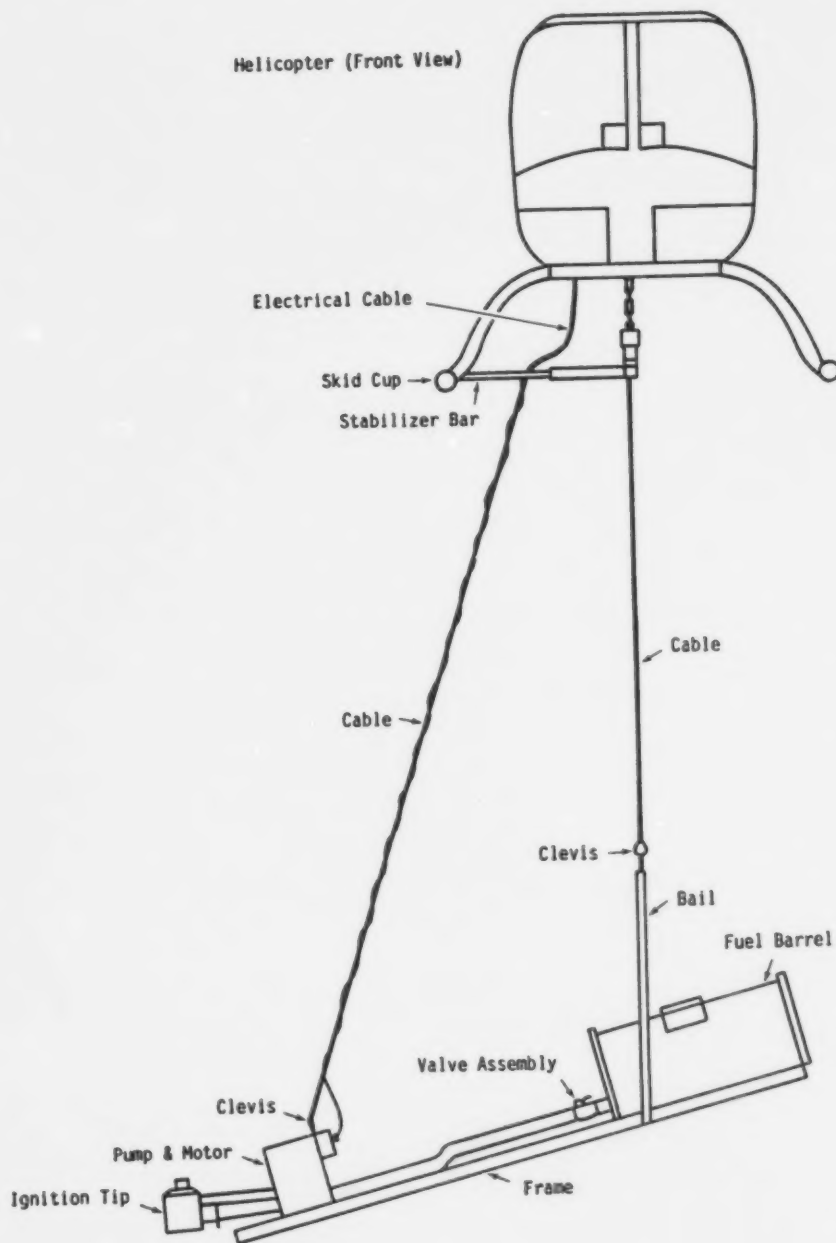


FIGURE 4 PRIMARY COMPONENTS OF THE SLING-LOADED HELITORCH IGNITION DEVICE

up to 30 seconds. By varying the grain size and the volume of potassium permanganate, one could seek the optimum reaction and flame size for varying needs. The chemical composition used for AID deployment on land is clearly not appropriate for the ignition of oil slicks. Numerous tests have been conducted with the AID on water in its present configuration. In all tests, the igniter is easily doused and sunk if water is splashed into the burning ball. With minor modifications, however, it may be possible to utilize an AID-like device as the starter for an attached component capable of sustaining a long-burning, high-intensity flame.

Another very appealing aspect of the Premo AID approach is the dispenser that has been developed for rapid deployment of the devices from a helicopter. The dispenser has evolved to the Mark III version depicted in Figure 5. Its primary function is to inject a controlled amount of glycol into each AID, thereby initiating the exothermic reaction, and then to expel the primed devices at a very high rate. The dispenser is constructed of welded aluminum, and it is shaped to accommodate the rear door sill of a Bell 206 helicopter. Auxiliary support brackets for attachment to other helicopters are available from the manufacturer.

Inside the AID dispenser are four chutes that feed the devices from the storage hopper into four separate chambers. Within these chambers, the igniters are sequentially injected with the glycol and then immediately ejected from the exit chute at the bottom. The maximum ejection rate is 3 igniters per second when the dispenser is operated with the exit chute fully open and with its camshaft speed at its highest setting. The dispenser also contains a water reservoir that feeds an internal fire-extinguishing system in the event of any malfunction within the unit. Held in place with tie-down straps and operated with a quick break-away connection on its power cable, the dispenser can be jettisoned quickly in an emergency.

The entire AID dispenser, including full hopper (450 AID devices), full glycol tank (9 liters or 2.4 U.S. gal), full water tank (3 liters or 0.8 U.S. gal), and all accessories, weighs just under 45 kg (100 lb). The dispenser is approximately 69 by 28 by 66 cm in length, width, and height; and it can be operated with a 12- or 24-volt DC power source.

SUMMARY EVALUATION

Table 1 covers 30 carefully selected assessment criteria grouped under the categories of safety, storage, government regulations, availability, cost and operational considerations. These criteria are addressed for the two proven pyrotechnic devices currently available; for the laser ignition system, which is still in an early experimental stage; and for two systems that are well-developed and proven techniques for initiating burns on land, but have never been tested for the ignition of floating oil slicks. For a detailed assessment of the operational considerations associated with each ignition system, the reader is referred to the original report (Spiltec, 1986).

From a safety standpoint, none of the igniters present any serious threat to human life and equipment due to open flames or sparks onboard the aircraft being used. All igniter concepts, except for the Helitorch, have a very low susceptibility to any accidental activation. Once in flight, the Helitorch is also quite safe with respect to the pilot and helicopter; however, there must be an unusually strict set of guidelines for the safe

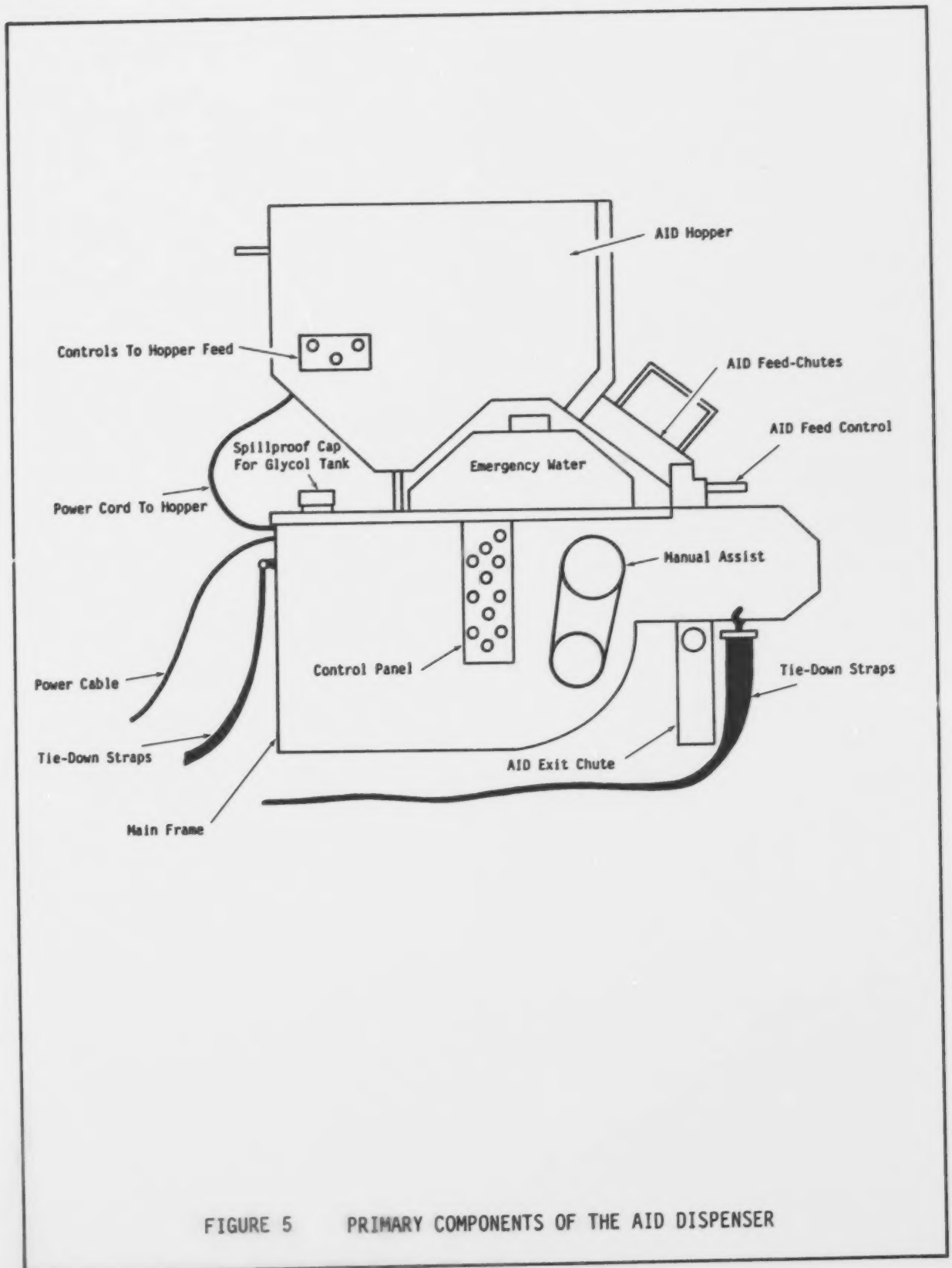


FIGURE 5 PRIMARY COMPONENTS OF THE AID DISPENSER

TABLE 1
SUMMARY OF IGNITER CHARACTERISTICS AND PERFORMANCE

ASSESSMENT CRITERIA	EPS IGNITER	DOVE IGNITER	LASERS	HELITORCH [®]	AID-LIKE DEVICES ^{**}
SAFETY					
Open flame or sparks inside aircraft	None	None	N.A.	None	None
Susceptibility to accidental activation	Highly unlikely (requires removal of safety pin)	Highly unlikely (requires separate ignition source)	Highly unlikely (positive off/on control)	Unlikely (positive off/on control)	Unlikely (chemical starter probably isolated from fuel)
Retrieval and handling of igniters that have misfired	Safe to handle after 2-min. delay	Safe to handle after 2-min. delay	N.A.	N.A.	Uncertain
STORAGE					
Shelf life	5 years	5 years	N.A.	N.A. (Flammable mixture prepared at time of need)	Indefinite
Difficulty of replacement (all or in part) following normal shelf life	Relatively simple replacement of pyrotechnic portion only (about 25% of initial cost)	Relatively simple replacement of pyrotechnic portion only (about 50% of initial cost)	N.A.	N.A.	N.A.
Routine maintenance requirements	None	None	Minimal	Minimal (pump, valves, stirring equipment, etc.)	Minimal (moving parts)
Susceptibility to high or low temperatures during storage/transit	Very low (tested between -58°F and +122°F)	Very low (tested between -76°F and +122°F)	Currently under investigation	Gel-mixing process best carried out at or above freezing air temperatures	No anticipated concerns
Susceptibility to vibration or humidity during storage/transit	Very low (meets military requirements)	Very low (meets military requirements)	Currently under investigation	Vibration - No problem. Must keep gel-mixing process free of water	No anticipated concerns
GOVERNMENT REGULATIONS					
Shipping and storage restrictions	Basically treated as fireworks. Housed and locked in non-sparking container, properly marked as fireworks. Shipment by land, sea or chartered aircraft permitted; shipment by commercial passenger aircraft prohibited.	Basically treated as fireworks. Housed and locked in non-sparking container, properly marked as fireworks. Shipment by land, sea or chartered aircraft permitted; shipment by commercial passenger aircraft prohibited.	Subject to Federal Aviation Regulations (Part 29) regarding "airworthiness" and ANSI Z136.1 regarding laser safety considerations, eye protection, etc.	Subject to same storage and transit requirements for petroleum products. Cannot fly Helitorch over populated areas. (FAA Part 137 approved)	Requirements should be even less restrictive than for EPS and Dome Igniters. Components kept separate.

* Or comparable system involving the continuous spraying of a burning fluid or gelled substance

** Continuous automatic ejection of modified Premo AID-like igniters with delayed-reaction chemical starters (final concept yet to be designed and tested)

TABLE 1 (Cont'd)

ASSESSMENT CRITERIA	EPS IGNITER	DOSE IGNITER	LASERS	HELITORCH [®]	AID-LINE DEVICES
AVAILABILITY					
Currently stockpiled	All stockpiles currently depleted	Approx. 1,700 igniters, Prudhoe Bay (owned by Alaska Clean Seas); approx. 4,000 igniters at Tuktoyuktuk, Canada (owned by Dome)	Current laser system is experimental only	Numerous units available in U.S. and Canada	None (under development)
Resupply capability	Typically 2,000 to 3,000 igniters per month once raw materials on hand	Typically 4,000 to 6,000 igniters per month once raw materials on hand	Current laser system is experimental only	Under emergency conditions, approx. 20 Helitorch [®] per month	None (under development)
COST					
Estimated cost (\$U.S./igniter) at factory	\$80 to \$100 (depending on volume purchased)	\$40 to \$60 (depending on volume purchased)	\$ $\frac{1}{2}$ million to \$3/4 million	Approx. \$4,000 per application unit. Approx. \$20 to \$25 for gelling agent per drum of gasoline (or gasoline/diesel mix)	Uncertain
OPERATIONAL CONSIDERATIONS					
Level of field testing performed to date	Moderate. Mostly small controlled spills	Extensive. Many controlled spills and some actual spills	Static, small-scale tests only. No helicopter-mounted tests yet	Extensive experience on land. No experience with oil on water	Small-scale testing of AID alone on water. Final concept unproven
Reliance upon unique airborne application device	None	None	Yes. Continuous-wave CO ₂ laser plus a high-powered pulse laser	Yes. Helitorch frame and pump assembly	Yes, possibly similar to Premo AID system (may also have hand-release capability)
Igniter (and/or application system) preparations--from storage to field use	None	None	Extensive. Mounting brackets, auxiliary power, focusing/stabilizing equipment, and calibration	Minor setup. Self-contained package quickly prepared and sling-loaded	Likely minor setup. Self-contained unit should be quickly installed
Average rate of application	Approx. 3 to 6 per min.	Approx. 3 to 6 per min.	Approx. 1 to 2 ignition attempts/min.	Burning globules (golf ball size) over a swath 10 ft wide typically about 1-mile-long runs per sortie at 25 to 30 mph and at 50-ft altitude or less	Unknown
Approximate number of igniters releasable per helicopter sortie	Typically 50 to 100 depending on helicopter selected and ability to set down for transfer of cargo to passenger area	Several hundred depending on helicopter selected and ability to set down for transfer of cargo to passenger area	N.A.		Unknown
Accuracy of deployment on target oil slick	Good. New design reduces tendency to roll. Still may bounce/skip on ice. Some drift while airborne	Excellent. Irregular shape prevents rolling. Low drift while airborne	Excellent (Assuming stabilization, focusing, and range requirements are met)	Random distribution of burning gel over target area	Possible random distribution of seal and inexpensive igniters
Durability (or resistance to damage during impact)	Good. Designed for typical drop heights of 50 to 100 ft onto frozen surface	Good. Designed for typical drop heights of 50 to 100 ft onto frozen surface	N.A.	N.A.	Anticipate light, durable igniters

* Or comparable system involving the continuous spraying of a burning fluid or gelled substance
 ** Continuous automatic ejection of modified Premo AID-like igniters with delayed-reaction chemical starters (final concept yet to be designed and tested)

TABLE 1 (Cont'd)

ASSESSMENT CRITERIA	EPS IGNITER	DOME IGNITER	LASERS	HELITORCH*	AID-LIKE DEVICE**
Performance in shallow pools (less than 4 in. deep) on solid ice	Good. Shallow draft	Good. Shallow draft	The feasibility of heating and then igniting an oil layer under actual arctic conditions with currently available commercial lasers is being investigated by Environment Canada. Statinary tests on small controlled slicks have been conducted satisfactorily and look very promising.	Experience to date suggests that the deployment of a Helitorch system may provide a means of igniting oil stranded on ice, in shallow melt pools, and possibly on deeper water. Celled mixtures can be created to give varying sizes and distributions of burning globules that can float and burn for several minutes.	The AID-like device may serve as an effective, self-destructive starter for any number of flammable mixtures that could be attached to the starter and released into the surrounding oil upon ignition.
Dependence on orientation for proper performance	Either of 2 stable, floating positions	Either of 2 stable, floating positions			
Nature and orientation of flame during ignition of oil	Symmetrical 360° burn from perimeter of igniter radially outward. Lightly pressured flame parallel to water/oil surface	Soft, billowy flame concentrated over oil/water surface between floats			
Splash effects during impact with oil and water	Significant, though oil layers greater than 1/10 in. quickly become re-established around igniter	Significant, though oil layers greater than 1/10 in. quickly become re-established around igniter			
Temperature and duration of heat source	2,550°F to 4,170°F for 2 min.	More than 3,700°F for 10 seconds followed by 2,200°F to 2,400°F for approx. 10 min.			
Reliability of starter	Typically greater than 95%	Typically greater than 95%			
Reliability of igniter	Typically greater than 75% (begins to drop after 5-year shelf life)	Typically greater than 90% (begins to drop after 5-year shelf life)			
Sensitivity to temporary submergence upon impact	None	None			
Sensitivity to wind, rain and sea state during ignition	Low	Low			
Type and amount of debris after use	Small metal firing mechanism survives fire, but sinks	Entire metal float package and fuel basket survive fire and remain on water surface	No debris	No debris	Should be no debris
Training requirements	Minimum (about 10 min.). Experience needed in identifying and hitting appropriate "targets"	Minimal (about 10 min.). Experience needed in identifying and hitting appropriate "targets"	Extensive training and field experience required	Extensive training and field experience required	Moderate level of training anticipated

* Or comparable system involving the continuous spraying of a burning fluid or gelled substance

** Continuous automatic ejection of modified Premo AID-like igniters with delayed-reaction chemical starters (final concept yet to be designed and tested)

mixing of highly flammable liquids and their transfer between containers onsite. Particular care must also be exercised in selecting a flight path with a sling-loaded cargo of flammable liquid.

One particularly good point about the Helitorch and laser concepts is the fact that there is no need to be concerned about the handling of an igniter that has been released and which has failed to burn. In the other systems there is the remote possibility that an unactivated unit might drift and be retrieved by someone who is unfamiliar with the potential dangers of the unit. This concern may be of particular importance in the event that many hundreds or thousands of units are deployed over a large spill area. In most cases the device would normally be safe to handle by experienced personnel within a very short period (normally less than 2 minutes). And, in cases where the unit was not retrieved immediately, sea-water exposure would normally render the unit safe for handling by almost anyone within a matter of hours.

Another important difference between the units involving pyrotechnic devices and those not containing such components is the fact that the pyrotechnic components will almost always become less reliable with time, particularly as the system's shelf life is approached. Should it be necessary to store large numbers of igniters, the cost and inconvenience of having to replace a portion of every igniter every 5 years could become a very significant concern. The laser, Helitorch, and AID-like ignition concepts could eliminate much, if not all, of the usual storage and handling costs. These concepts may also require much less time, effort, and money for complying with government regulations associated with explosives storage and transport.

The availability issue is probably the most important factor for deciding what will be used in the event of a spill or stockpiled prior to a spill. Currently, the only proven igniter for floating oil slicks that is stockpiled in the U.S. and Canada is the Dome igniter. This igniter is also the only one for which raw materials are immediately available and for which emergency manufacturing could be started almost immediately. The Dome igniter also costs about half as much as the other proven pyrotechnic igniter.

If an effective system can be developed involving lasers, the Helitorch, or an AID-like device, such an ignition concept would play an important role in supplementing the existing technology using pyrotechnics. Individual, hand-thrown igniter packages that are relatively bulky and expensive may be satisfactory now for a number of potential spill scenarios. However, a shift toward unique airborne application devices using focused "energy beams" or very small and inexpensive ignition devices could result in improved performance and savings in time and money. Particularly where the targeted oil slicks consist of numerous, small, closely spaced oil concentrations, the most cost-effective mode of ignition may involve the random broadcasting of an ignited gel or of numerous mini-igniters from an automated dispenser. In this latter mode of distributing igniters, considerable effort and time can be saved by not having to (1) create and maintain large inventories and storage areas, (2) transport such inventories to an appropriate staging location, and (3) land or return to base as often to rearrange or pick up igniters.

The rate at which individual ignition points can be achieved is quite important recognizing the limited time that might be available for completing an in-situ burn operation. This time would obviously depend upon many factors including the number and spacing of slicks; their distance from staging locations; their exposure (say, through melt pools in spring) and residence times (due to evaporation, ice movement, etc.); and the weather conditions. However, be it 10 hours or 10 days, one can envision any number of spill situations where the ignition of only a few pools of oil per minute may reduce the burning program to a selection of only the largest pools of oil within the time available. And because of the possible rapid changes in weather and ice conditions, it is not always possible to anticipate the time that will actually be available to reach and ignite a large field of oiled ice.

The average rate of deploying hand-thrown devices (including activation of the starter, aiming, release, and repositioning of the aircraft for the next slick) is generally expected to be between 3 and 6 igniters per minute. A laser ignition system, subject to the current requirements for preheating and ignition, would likely run between 1 and 2 ignitions per minute. And, the AID-like approach could possibly result in many 10's of ignitions per minute. This latter approach is in the early stages of evaluation and is therefore very difficult to assess. It is also hard to anticipate the number of actual successful oil pool contacts and ignitions that might result using such a random broadcasting technique. Development work scheduled for 1986 may reveal that if such devices are feasible, it may be possible to develop a rapid-fire dispenser that also can be stopped and started quickly and that can be aimed. This would reduce the number of igniters wasted during an otherwise random-toss mode.

All of the igniter characteristics and operating considerations discussed so far are, of course, important in the selection of a cost-effective ignition system now and for future operations. A most significant area of consideration, however, is the performance of an igniter in presenting sufficient heat long enough and over enough area to ignite and sustain an in-situ burn that can propagate over the entire slick. The success with which an entire slick is consumed is not just related to the performance of the igniter, but more to the thickness and age of the oil being burned and to the placement of the igniter. Even moderate winds in the 10- to 15-kt range have been observed to prevent the upwind propagation of flame over a slick.

The two pyrotechnic devices developed by the EPS and Dome Petroleum Ltd. have been used repeatedly on a variety of oil slicks to demonstrate their effectiveness in igniting and sustaining proper in-situ burns. While the EPS igniter burns a bit hotter than the Dome igniter, the EPS device provides an exposure to flame of only about 2 minutes. The Dome igniter flashes with intense heat (about 2,000°C) for about 10 seconds, followed by approximately 10 minutes of continuous flame in the 1,200°C to 1,300°C range. This extended exposure period can be the difference between success and failure in situations where the oil around the igniter may not be sufficiently thick to support combustion. As winds or currents act on the surface slicks, the volume of oil immediately around the burning igniter may build until, after a few minutes, the thickness is suitable for a self-sustaining fire.

Both of these hand-thrown igniters are subject to problems that can arise when winds are sufficient to remove the vapors (produced during the preheating phase) so rapidly that they cannot be ignited or they are rapidly blown out. The Dome igniter, with its fuel basket suspended between the floats, tends to reduce the potential for this problem by trapping oil and vapors between the floats. It has also been observed during tests with the igniters (and with various types of weed burners), that the "softness" of the flame produced is critical in allowing for a proper heat exchange between the fire and the oil. If the flame is too forceful (as if blown from gas jets) out toward the oil layer, it simply pushes the oil layer away. If, on the other hand, the flame is relatively "soft" and unpressured, the oil can settle around or beneath the flame allowing for a rapid volatilization of the oil and for subsequent ignition.

It is this need for a relatively long (i.e., several minutes) exposure of oil to an intense though "soft" flame that may introduce some of the real-world difficulties in perfecting the laser-induced ignition of oil. The self-sustaining properties of the initial flame produced by the pulsed laser may not be sufficient to overcome the dissipative influence of even a light wind. For totally exposed slick surfaces (i.e., no surface obstructions for the wind), the laser ignition system will have to overcome the negative influences of heated oil moving away from the irradiated surface area and of released vapors being blown away.

An effective ignition system must reflect the importance of a balanced flame intensity, duration, and "softness" for successful ignition under most conditions. It may be desirable, for example, to combine the target-selection capability of a hand-thrown unit, and the intensity- and duration-of-burn properties of gelled gasoline/diesel with the safe and simple delayed reaction of a chemically induced starter. By encouraging the mixing and spreading of the gelled medium with the target oil slick, it may be possible to considerably enlarge the area of influence during ignition.

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THE MINUK I-53 ARTIFICIAL ISLAND OIL SPILL

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SPILL INCIDENT/RESPONSE

As a result of an intense storm which occurred in the southern Beaufort over a three day period (September 15 - 18, 1985), Esso Resources' artificial island Minuk I-53 was severely eroded and effectively moved 90 meters to the east, with material being picked up from the western segment and deposited to the east by the wave action. While all personnel were safely evacuated, the rig's derrick collapsed, the camp was lost, a considerable quantity of drilling material stored on the island was washed away, and diesel fuel tank was undermined and toppled into the water. A spill of 388m^3 (2440 bbls.) of P50 diesel subsequently occurred.

The resulting slick was first observed a few hours later approximately 6km east of the island (Fig. 1). It was being driven by strong westerly and later southwesterly winds. At the next siting, five hours later the same day, the slick had moved 24km northeast of Minuk, with dimensions of 4.8km long by 1.5km wide. A final siting that day revealed that the slick had turned to the northwest in response to a wind shift.

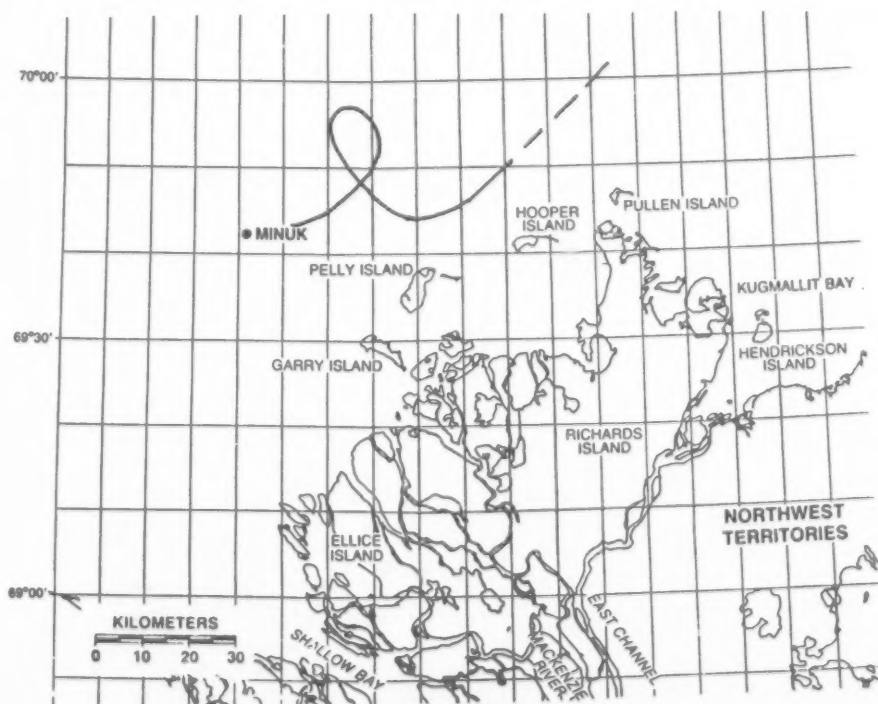


FIGURE 1
MOVEMENT OF MINUK DIESEL SPILL

A series of spill fate and movement models were initiated by Esso which indicated that significant evaporation and natural dispersion into the water column were occurring during the first few hours, due to the volatility of the product and the high surface energies (Table 1).

TABLE 1
FATE OF MINUK DIESEL SPILL

TIME HOURS	EVAPORATION %	DISPERSION %	DISSOLUTION LT 1%	ON SURFACE %
1	4	3		93
2	10	6		84
3	15	10		75
6	23	18		59
12	30	30		40
24	35	44		21
36	36	51		13
48	37	55		8
60	38	57		5
72	38	58		4
78.8	38	58		4

The slick was next observed the morning of the second day at first light approximately 32km northeast of Minuk (Figure 1). It had spread to a 6.5km by 3.2km sheen with a thicker lens in the centre. Some of the product had started to emulsify. At this time two tracker buoys from the Beaufort Sea Oil Spill Co-op were deployed by helicopter into the slick.

Winds were projected to move back to the northwest, and the trajectory models which were being run at Esso's Research Laboratories in Calgary on a regular basis, indicated that diesel could come ashore, or close to Pelly and Hooper Islands, based upon the 24 hour forecast (Figure 2).

MINUK DIESEL SPILL TRAJECTORY

FORECAST: SEPT. 19 0600

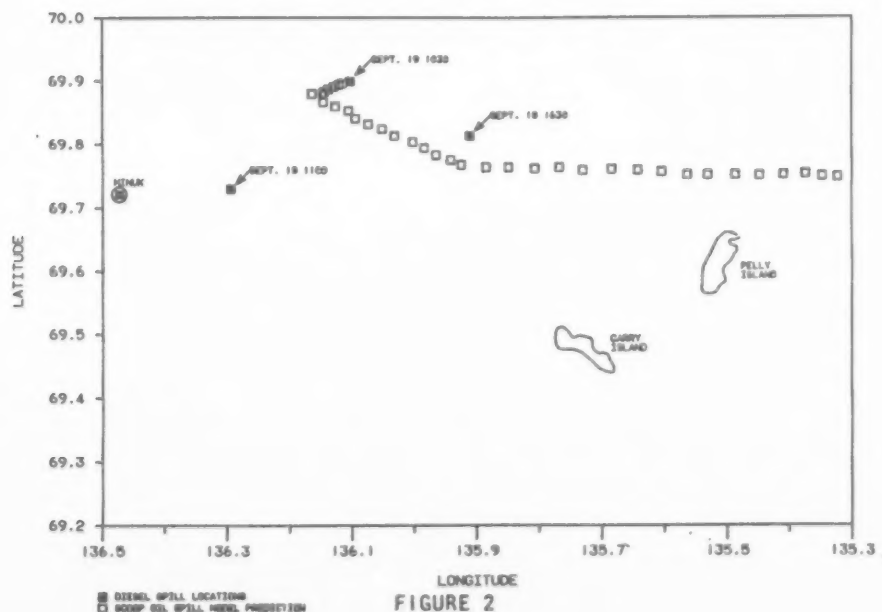


FIGURE 2

Plans were therefore made to apply dispersants to any slick which might approach land, as this was both the Government's and Esso's primary concern because of the use of such shorelines along the Barrier Islands for nesting and migrating waterfowl. Approvals were sought and obtained from the government, through the Canada Oil and Gas Lands Administration (COGLA) to use dispersants if necessary. Dispersants and a helicopter boom/bucket system were made ready at Esso's Tuk Base.

Prior to this the Beaufort Sea Oil Spill Co-op had been put on standby as soon as it was evident that one or more diesel tanks on the island might be damaged. It was recognized however that physical containment and recovery of the product would be difficult during the storm and even after the weather improved as the slick would be very thin, as proved to be the case. The co-op did supply bladders, pumps, and hose for a transfer operation which took place on the island after the storm subsided to remove the remaining fuel in the event that further storms and erosion took place.

During the night of the second day following the spill the winds changed direction again and moved the remaining slick away from land. Subsequently the need to apply dispersants was reduced and efforts concentrated on monitoring the movement and fate of the slick. During the third day, an aerial surveillance flight located a signal from the tracker buoys in the area where Esso's trajectory models predicted the slick should be, at a location approximately 35km east of Minuk. However no visual contact of the slick was made from the helicopter.

By this time, a remote sensing system, using IR/UV detection was mounted into Esso's Twin Otter aircraft and the first flights using this equipment took place. After 2 hours of flying a grid pattern through the area, the remains of a slick (a sheen 16km long by 8km wide) with thickness varying from 10-50 microns, was found northeast of Pelly Island, approximately 8km from the nearest land. The total diesel estimated to be remaining on the surface by that time was $8m^3$ (50 bbls). The IR/UV system was subsequently used to survey all shorelines in the area for any presence of oil, with no product detected.

A final remote sensing survey was carried out in the morning of the fourth day, based on spill trajectory predictions as to the slick location. During an intensive grid flight pattern no trace of the slick was recorded, and it was agreed that the slick had evaporated and dispersed to the point where no significant amount remained on the surface. At this point the surveillance was terminated and the spill incident deemed to be over.

GOVERNMENT INVOLVEMENT

Canada Oil and Gas Lands Administration (COGLA) personnel had been monitoring the weather situation in the area and the effect on other drilling operations which were taking place at the time. These operations were providing daily reports by telecopier, as required. The Minuk operation was not providing written daily reports at the time because drilling operations had not yet begun.

Esso drilling personnel kept COGLA Yellowknife office informed of the progress of the storm and the effect on the island early in the emergency by telephone. COGLA continued to monitor the situation and informed other government departments of the potential emergency situation.

Prior to the oil spill taking place, COGLA declared a First Order Response, in order to more effectively keep senior management, other government departments and the public informed about the emergency.

In declaring the response, the Regional Emergency Response Team was set up, with daily briefings of concerned government agencies taking place. Also, the Environmental Advisory Team was set up to provide advice to COGLA and Esso on wildlife and habitat as well as weather and oceanographic conditions. Members of this environmental team were located in Yellowknife, Edmonton and Pat Bay, British Columbia.

The Environmental Team recommended that critical bird habitat on the barrier islands be protected from diesel fuel spilled. The team also provided information on bird species expected to be in the area at the time, oil spill trajectories, and dispersant effectiveness on spilled diesel.

The spilled fuel at one time looked as if it could come ashore on one of the Barrier Islands. Given this potential, Esso forwarded a request to Environment Canada, through COGLA, to use dispersants on the fuel should the need to do so arise. The request to use dispersants was forwarded to Environmental Protection Service in Yellowknife, which provided approval-in-principle within a few hours to do so. Some conditions for their use and comments on their effectiveness were provided the next day. Dispersants were not used on the spill because the slick eventually moved offshore and broke up.

During the emergency, COGLA personnel were on site to assist Esso and to provide senior government management in Yellowknife and Ottawa with a first-hand evaluation of the situation. When the slick finally totally evaporated and dissipated, Esso and COGLA evaluated the situation and recommended that the emergency response, related to the spilled oil, be terminated. Based on these recommendations, the emergency response was declared over and follow-up post-briefing and reporting took place.

OIL IN PACK ICE:
PRELIMINARY RESULTS OF THREE EXPERIMENTAL SPILLS

by

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INTRODUCTION

The behaviour of oil spilled in pack (or broken) ice has been the subject of research and study over the past decade (Ramsier et al 1973, Jerbo 1973, Martin 1976, Deslaurier et al 1977, Deslaurier 1979, Metge and Telford 1979, C-CORE 1980, Free et al 1982, S.L. Ross 1983, Fingas 1984 and Tebeau et al 1984). Prior to this experiment, however, no field spill data existed which could validate the results of small scale test tank work or verify various spill behaviour theories.

OBJECTIVE

The objective of this study was to investigate the physical and chemical fate of crude oil spilled among pack ice.

Goals

More specifically the study was designed to:

1. relate oil spreading behaviour to ice conditions ranging in concentration from 5 to 9 tenths,
2. evaluate the fate of oil spilled in pack ice by monitoring the processes of evaporation, emulsification, dispersion and incorporation into or on top of the ice, and
3. identify possible countermeasures strategies.

METHODS

On March 9 and 10, 1986 three spills of 1 cubic metre each of Alberta Sweet Mixed Blend crude oil (Table 1) took place approximately 140 km east of Chedabucto Bay, N.S..

TABLE 1

PROPERTIES OF ALBERTA SWEET MIXED BLEND CRUDE OIL

Density at 0°C:	0.8566 g/cm ³
Density at 15°C:	0.8448 g/cm ³
Viscosity at 0°C:	43.7 cP
Interfacial Tension:	
Air/Oil:	25.7 dynes/cm
Oil/Seawater:	19.0 dynes/cm
Oil/Water:	26.2 dynes/cm
Pour Point:	-80°C
Flash Point (closed cup):	70°C

Environmental conditions for each of the spills are summarized in Table 2.

For the first spill, in 3 to 5 tenths ice, one cubic metre of oil was transferred from drums on the deck of the M.V. Brandal (Plate 1) to a plastic bladder mounted on a raft (Plate 2). The raft was then slung over the side of the ship and placed in the centre of the test area (Plate 3). The bag was slit open to release the oil after the ship has moved away from the raft and the ice had returned to normal (Plate 4). For the second two spills the drums were tipped from an ice floes edge (Plate 5.) Two Zodiac inflatable boats (Plate 6), powered by 10HP outboard motors, were used to take oil samples and ice measurements. These proved to be surprisingly manoeuvrable in pack ice. An underwater video camera was used to document subsurface oil-ice interactions.

A Bell 206 helicopter was used as a remote sensing platform (Plate 7). Sensors mounted on the helicopter included: a Barr and Stroud 1R-18 infrared video, a Low Light Level Television (L³TV) camera, a true colour 1/2 inch video system, a true colour 70 mm Vinten aerial camera and a UV filtered black and white 70 mm Vinten aerial camera (Plate 8). Coloured nylon circles were placed around each site to aid in aerial video and photo interpretation; a 10 mx1m coloured nylon swatch was placed on a centrally-located floe at each site for scale (Plate 9). Positions were determined by Loran-C receivers on both the ship and the helicopter.

Surface oil samples were taken at predetermined times and locations from both thick and thin portions of the slick using the Belore sampler (Belore and Ross 1982). The sorbent pads were placed in 500 ml glass jars containing 100ml of hexane, "killed" with mercuric chloride and sealed with Teflon-lined lids. Grab samples (125 ml) were also taken whenever possible and similarly stored. Evaporative loss was determined by comparing GC traces of the samples with a lab-weathered standard; oil concentrations were determined using UV-spectroscopy.

PRELIMINARY DATA

Ice Conditions

Spill One March 9, 1986. Ice concentrations were between 4/10 and 5/10 in the area of spill one. The ice was composed of grey white to thin 1st year ice. Ice floes ranged from small pancakes to large floes with dimensions on the order of 10 m x 5 m. Ice thicknesses in the centre of the large floes were from 50 to 105 cm. Freeboard around the flow perimeters ranged from 5 to 44 cm. A thin crust of snow covered the floes. Slush ice filled the open water areas between floes at the start of the experiment.

Ice conditions during the experiment were very dynamic due to the proximity to the ice edge and the propagation of a 3-4 m swell through the ice field. As the experiment progressed conditions became more dynamic. By the end of the experiment the site was within several 100 m of the ice edge. At the ice edge the pack was rapidly broken up by the swell and large open water areas were exposed.

Water Temperature	-1.4 to -1.6°C
Oil Temperature	-1.0 to -1.5 °C
Ice Core Temperature	-2.2°C top to -1.3°C bottom
Sea Water Salinity	24 ppt (approximately)
Ice Core Salinity	0.5 ppt top to 5.0 ppt bottom

Spills Two and Three March 10, 1986. Ice conditions were 9+/10 in the areas of spills two and three. The ice was composed of young to thin first year ice in a state of moderate compression. Ice floes ranged from small pancakes to large floes with dimensions in the order of 28m x 16m. Total ice thicknesses ranged from 120 to 160 cm

TABLE 2
PRELIMINARY ENVIRONMENTAL DATA ON OIL IN PACK ICE SPILLS

SPILL NO.	ICE CONDITIONS (tenths)	OCEANOGRAPHIC CONDITIONS		METEOROLOGICAL CONDITIONS		
		SWELL	ICE DRIFT ^x	AIR TEMP. (°C)	WIND SPEED (km/hr)	WIND DIR'N (°T)
1	4-6 small floes and pancakes	3-4 m	1.1 km/hr to 140°T 1.9 km/hr to 158°T overnight	-8	35-45	270-285
2	7-8 medium floes surrounded by freezing brash	---	0.8 km/hr to 195°T	-14	30-35	310-335
3	4-6 medium floes surrounded by freezing brash	0.3-0.6 m (occasional)	0.7 km/hr to 155°T	-11	18-22	290-335

x from ship's LORAN

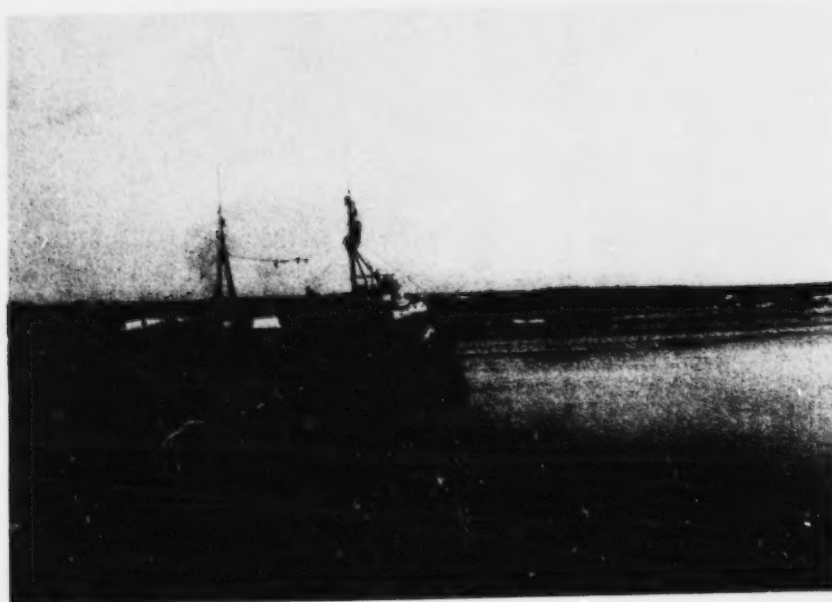


PLATE 1 - M/V BRANDAL



PLATE 2 - SPILL RAFT



PLATE 3 - PLACEMENT OF SPILL RAFT



PLATE 4 - OIL RELEASE, SPILL 1

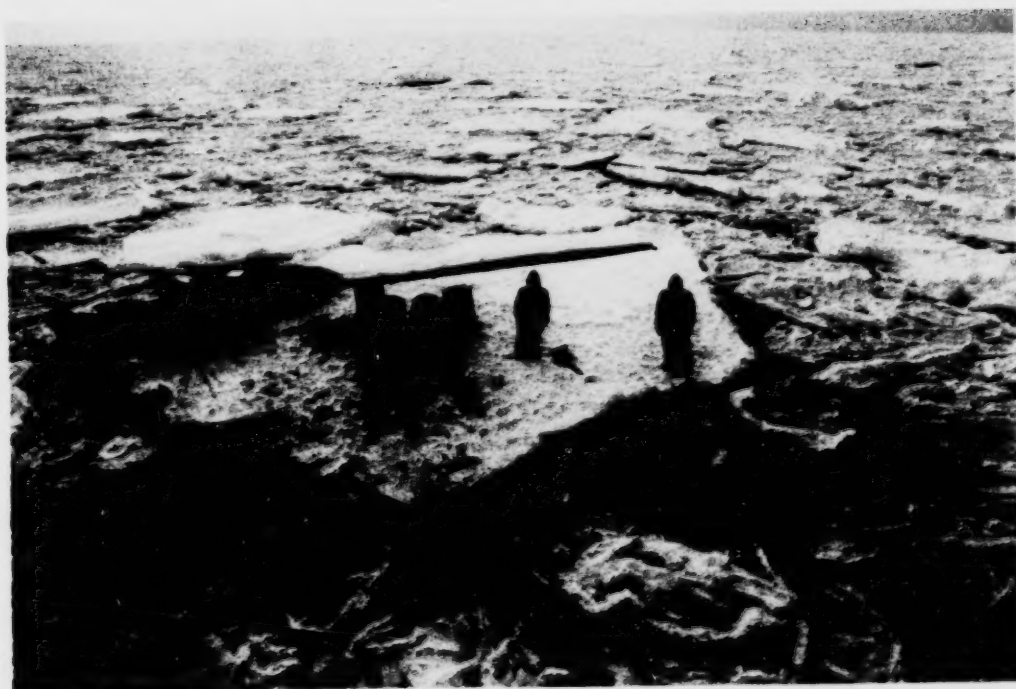


PLATE 5 - OIL RELEASED FROM DRUMS ON FLOE,
SPILL 3



PLATE 6 - SAMPLING BOATS



PLATE 7 - REMOTE SENSING HELICOPTER

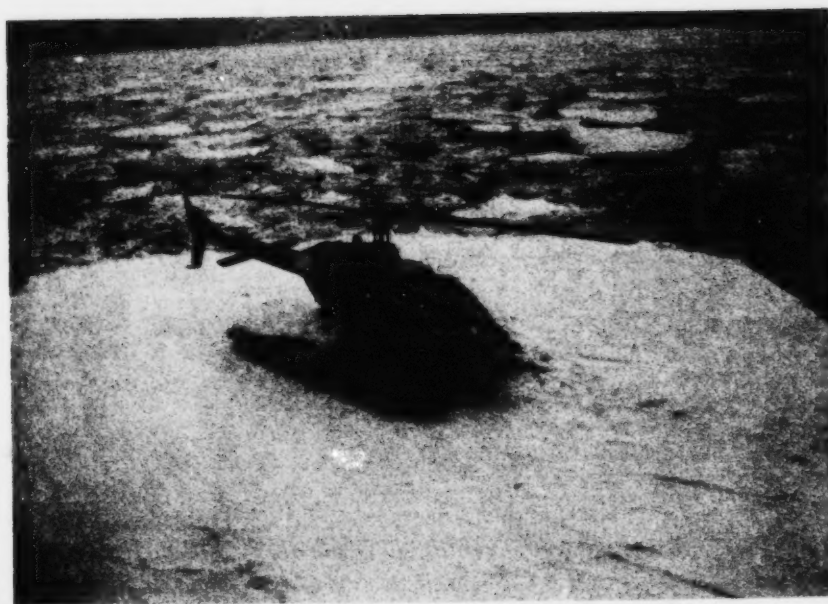


PLATE 8 - SENSORS MOUNTED ON STRUTS



PLATE 9 - COLOURED NYLON SWATCH FOR AERIAL PHOTO SCALE

with a layer of slush found at about 80 to 95 cm. Many floes were rafted and several underlying layers of ice were observed. Freeboard ranged from 5 to 52 cm. Snow cover on the floes was between 17 and 40 cm deep. Heavy slush ice up to 40 cm thick covered the leads between floes.

Ice motion during spills two and three was relatively static compared to the dynamic ice conditions observed during spill one. The swell was almost completely dampened. Leads opened by the passage of the ship closed rapidly in its wake. Relative motion between the floes was measured at about 20 cm over a 10 second period.

	Spill 2	Spill 3
Water/Slush Temperature		-1.7°C
Oil Temperature	-3.4°C	-3°C
Ice Core Temperature	-2.8°C top to -1.6°C bottom	

Oil Spreading

Figure 1 shows the results of a preliminary analysis of spill area (corrected to exclude ice) from the true colour 70 mm aerial photography. Also shown on Figure 1 is the theoretical spreading curve (Fay 1969) for the oil at 0°C on open water. The presence of high concentrations of brash ice in spills 2 and 3 dramatically reduced spreading. After 2 hours the oil in Spill 2 had only spread to an area of 30 m² with an equivalent thickness of 3 cm. The slightly lower brash ice concentrations in Spill 3 and the more dynamic conditions allowed the oil to spread to 70 m² (see Plate 5) in 30 minutes (yielding a thickness of about 1.5 cm).

In the lower ice concentrations of Spill 1, with only some brash ice present, and under the influence of very dynamic ice conditions (3-4 m swell) the oil spread to cover about 1x10⁵ m² after 3 hours with the thick slick covering about 4,000 m² of water. It was interesting to note that although the sheen, after 3 hours, had spread to cover a large area in the ice upwind of the release location as the pack drifted, the thick portion of the oil remained around the floes where it had been discharged. It thus seems that oil and ice floes both drift at the same rate under the influence of winds and currents.

Figure 2 shows the results of the thickness sampling of Spill 1. Samples were taken in the north end, centre and south end of the slick aligned with the northerly winds. Also shown for comparison is the theoretical prediction for the oil at 0°C on open water. The spill in open pack ice stays thicker for much longer than would be the case on open water. The data shown on Figures 1 and 2 indicate that the oil does go through a transition from gravity-viscous to surface tension-viscous spreading. The effect of the ice floes seems to be to delay the onset of the transition.

Evaporation

Figure 3 shows the evaporative loss for all three spills as a function of evaporative exposure (Stiver and Mackay 1983). Evaporative exposure is a dimensionless number that contains time, slick volume divided by area (i.e., thickness) and an air-side mass transfer coefficient. Also shown on Figure 3 are the results of artificial weathering of the crude oil by bubbling air through it at 20°C and the theoretical curves to predict evaporative loss derived from a modified ASTM distillation procedure (Stiver and Mackay 1983). The fit of the theory to the data is quite good considering the range of conditions over which the samples were collected (slicks ranging from 30 µm to 5 cm in thickness at -8 to -13°C offshore and a small scale laboratory test at room temperature).

FIGURE 1
OIL SPREADING IN PACK ICE

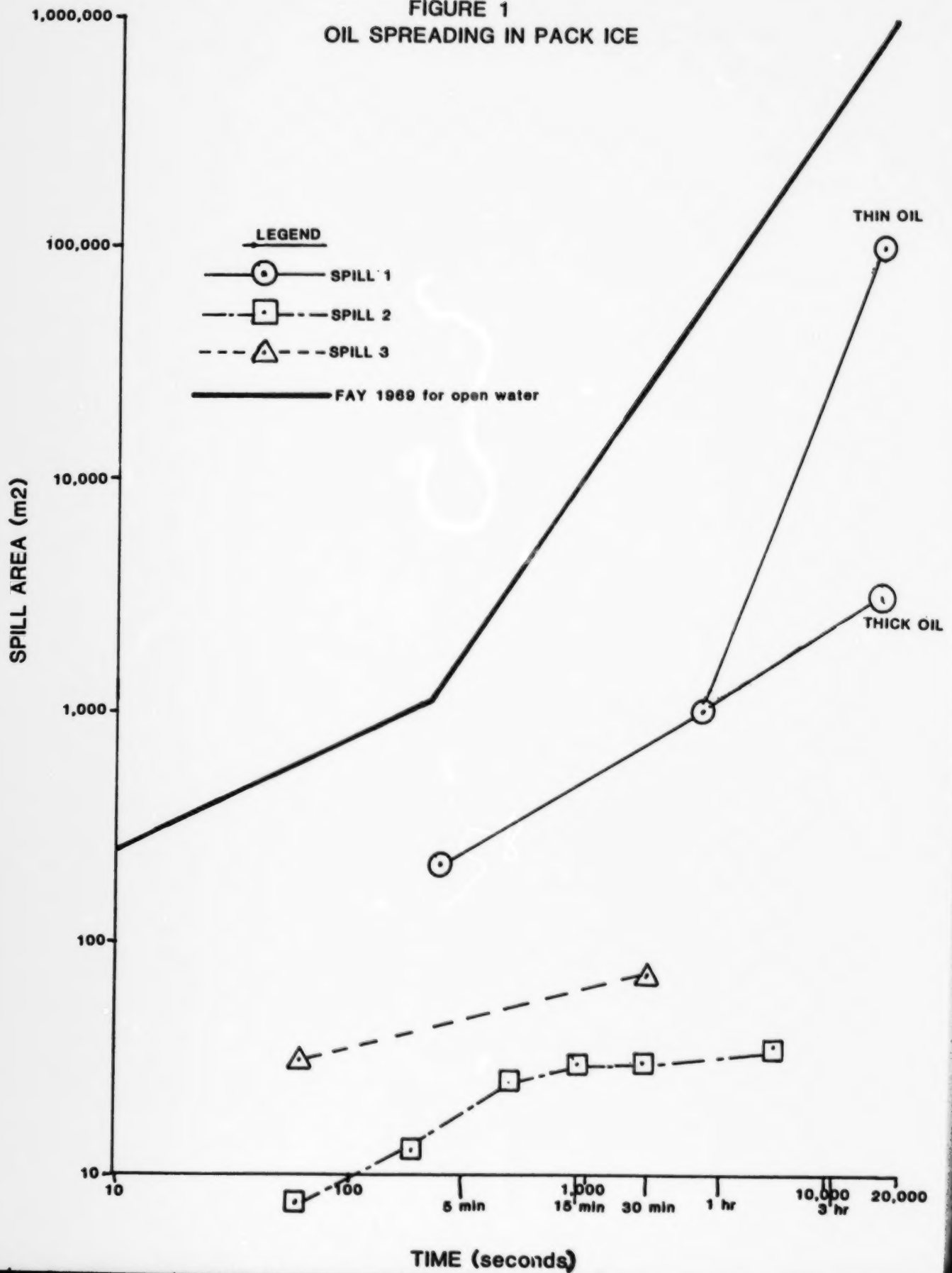


FIGURE 2
THICKNESS OF SPILL 1 vs TIME

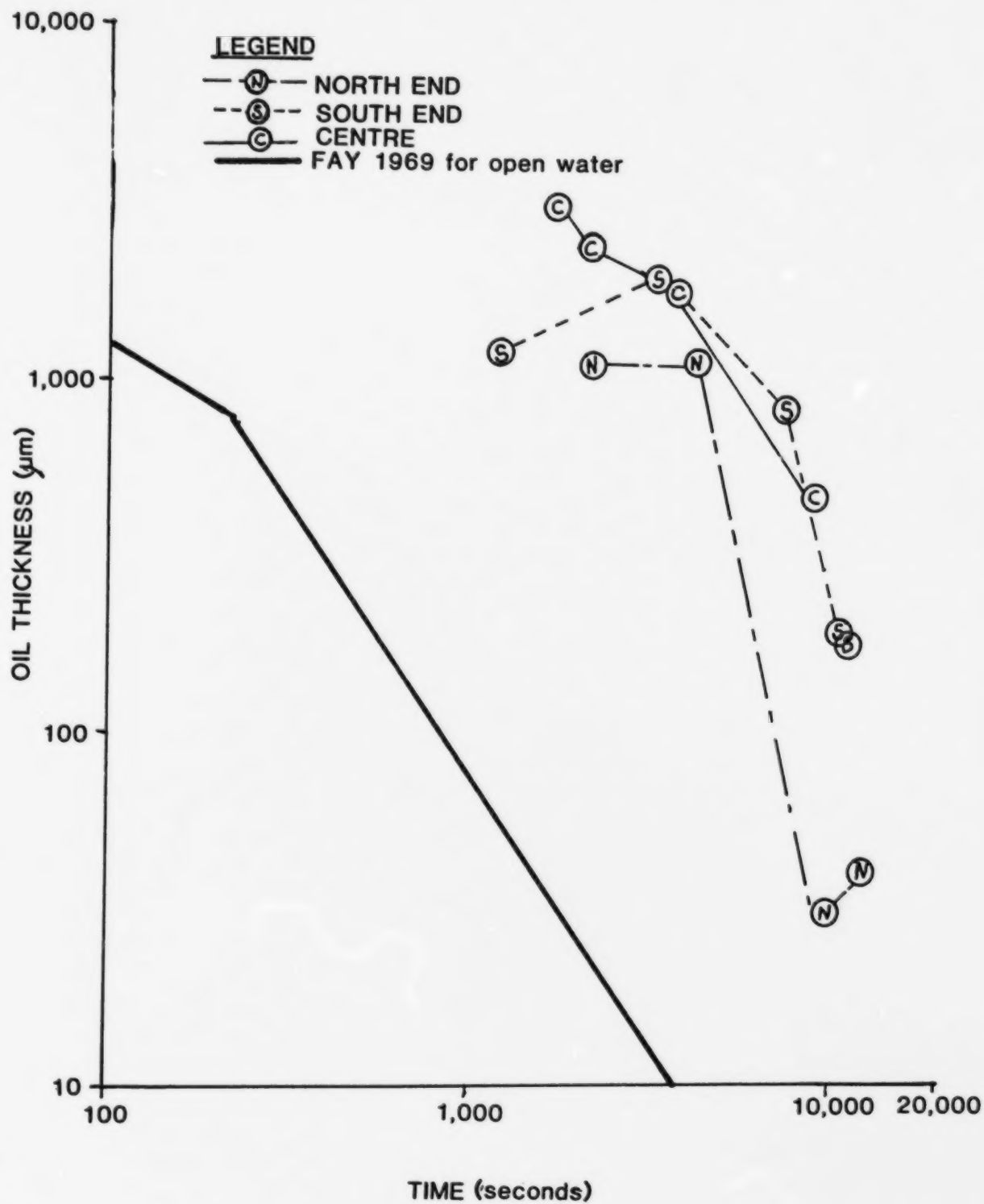
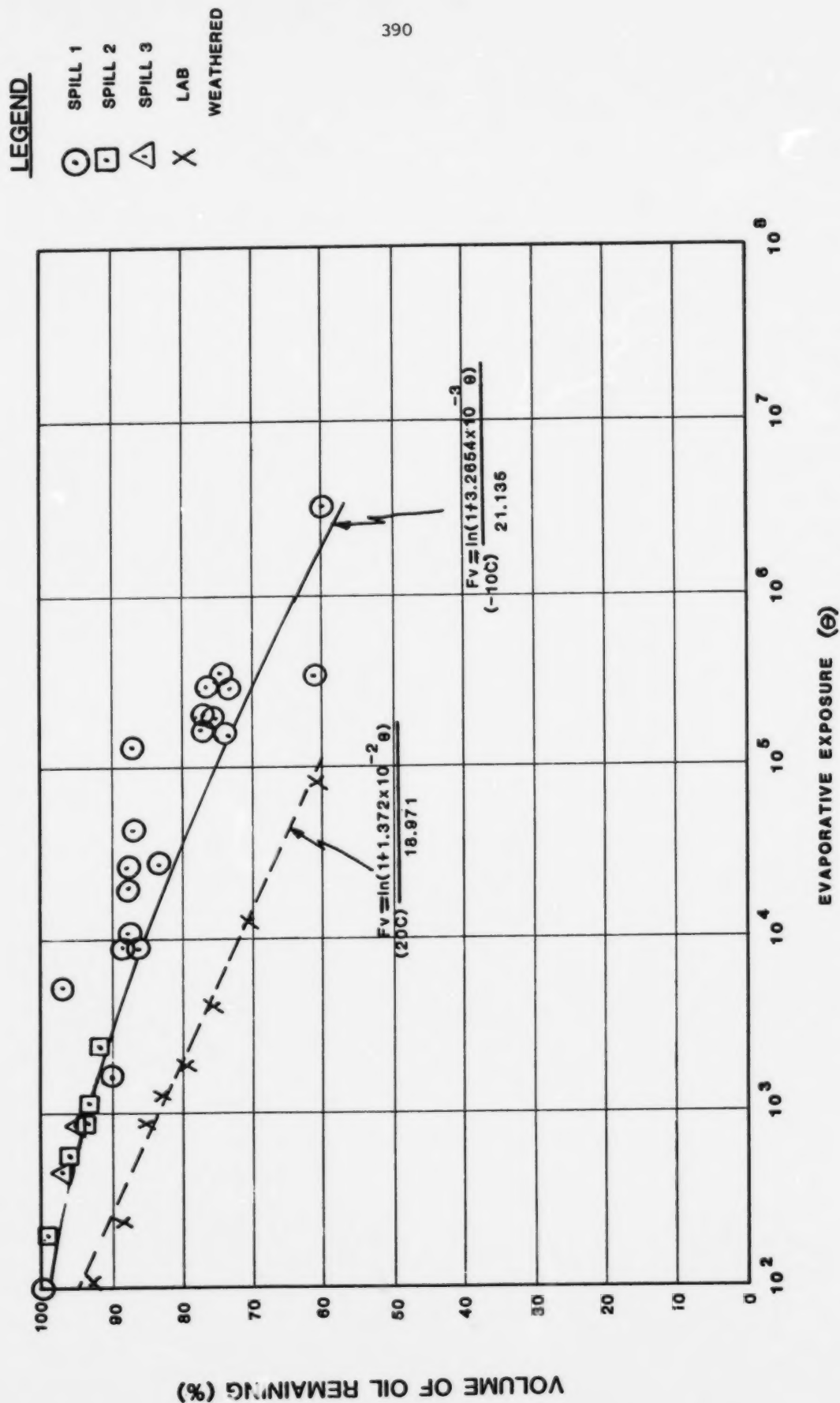


FIGURE 3 EVAPORATIVE LOSS



Weathering Effects on Oil Properties. Figures 4 and 5 show the effects of evaporation on the spilled oil's density and viscosity at 0°C. Also shown are the predictions of spill property models proposed by Mackay et al 1983. The properties of the oils in spills 2 and 3 changed little since the oil remained thick and concentrated.

Emulsification and Dispersion

No emulsification of the oil was observed to occur despite the dynamic conditions in Spill 1 and the fact that the oil is known to be prone to emulsification.

Though not measured quantitatively, underwater video at ice floe edges shows large droplets of oil being swept beneath the ice by currents. Visually, natural dispersion did not seem to be occurring at a significant rate. In 3-4 m seas in open water a slick such as Spill 1 would disperse rapidly; this was not the case in the pack ice.

Interaction With Ice

The oil interacted with the ice in three ways: it stained the brash ice surrounding floes, it splashed onto small pancakes of ice, and droplets were swept beneath floes by the currents.

The brash ice proved to be an effective barrier to limit the spread of oil; however, in dynamic conditions the oil eventually mixed with the ice to produce a brown slush which, with the rocking action of the floes, coated the outer rim of small floes and pancakes (Plate 10). In the less energetic conditions of spills 2 and 3 very little mixing of oil into brash ice occurred.

In spill 1 oil droplets, about 1 to 3 mm in diameter were observed being swept by currents beneath floes. A core sample from the floe showed that these droplets were trapped by the underside of the floe and had migrated some 25 cm up into the brine channels. Analysis of the melted cores showed oil concentrations of about 0.12 g of oil per L of melted ice, equivalent to an under ice oil thickness of approximately 150 µm.

Some oil was also found on top of the occasional pancake (Plate 11), though this was rare. One such sample scraped from the snow on a 1.3 to 1.5 m diameter floe contained 70 ml of oil per L of melted snow, an equivalent oil thickness of 250 µm. The oil was extremely weathered.

COUNTERMEASURES

Remote Sensing

Although all the remote sensing imagery has not yet been viewed, a preliminary assessment is that true colour video and photography and the infrared video are the most useful tools for documenting oil in pack ice. It proved impossible to detect the sheen with the UV filtered black and white photographs; the L³TV imagery has not yet been analyzed.

Physical Recovery

Although skimmers and pumps were aboard the ship they were never deployed. In the case of spill 1 the oil was too thin and widespread for skimming and attempts to concentrate it with booms would have been pointless because of the ice.

It would have been possible to skim or directly pump the oil contained by the ice in Spills 2 and 3 but it was simpler to just burn the oil. The residue from the spill 2 burn was picked up with shovels and placed in plastic garbage bags for disposal.

FIGURE 4
DENSITY vs EVAPORATION

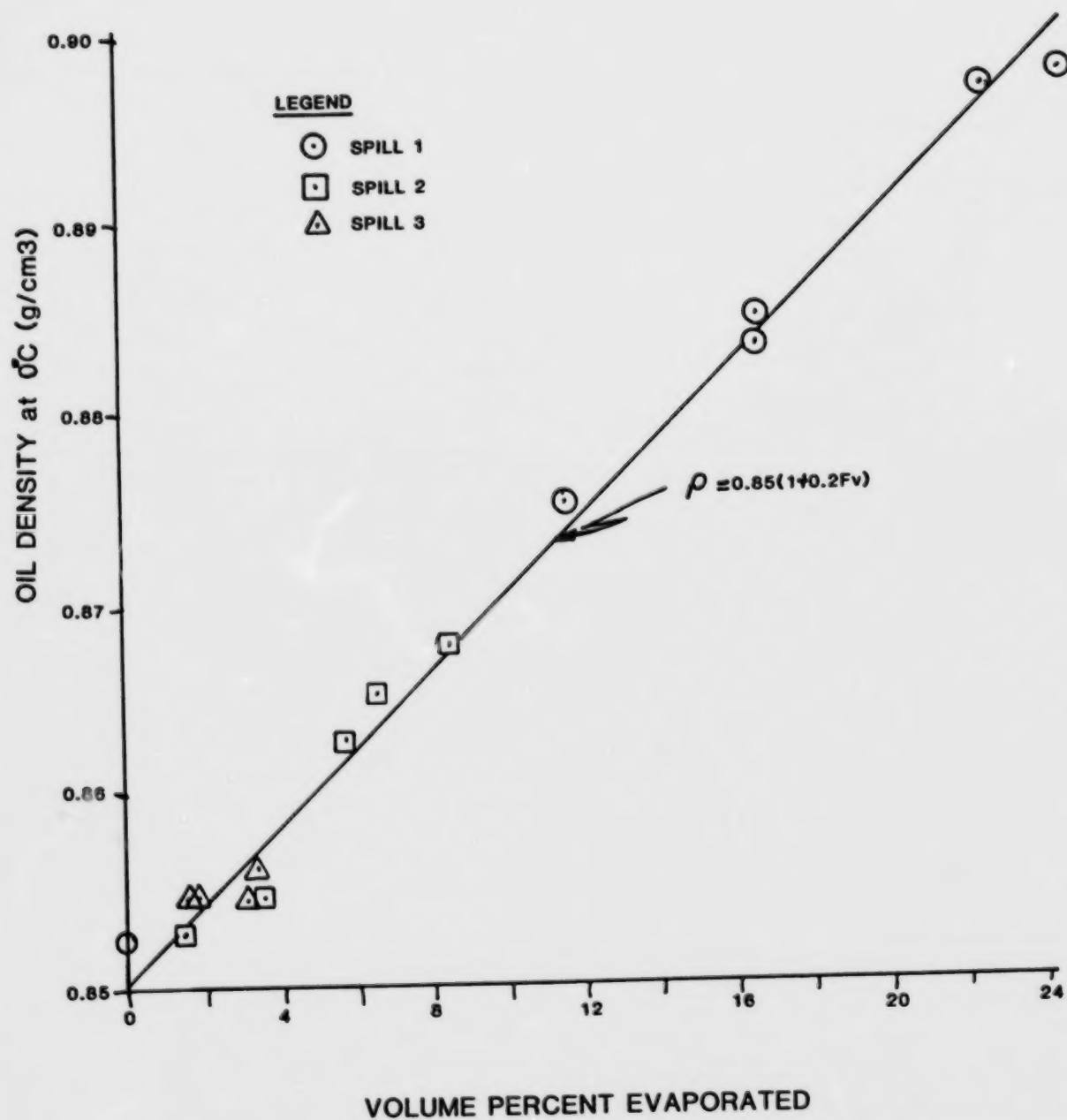
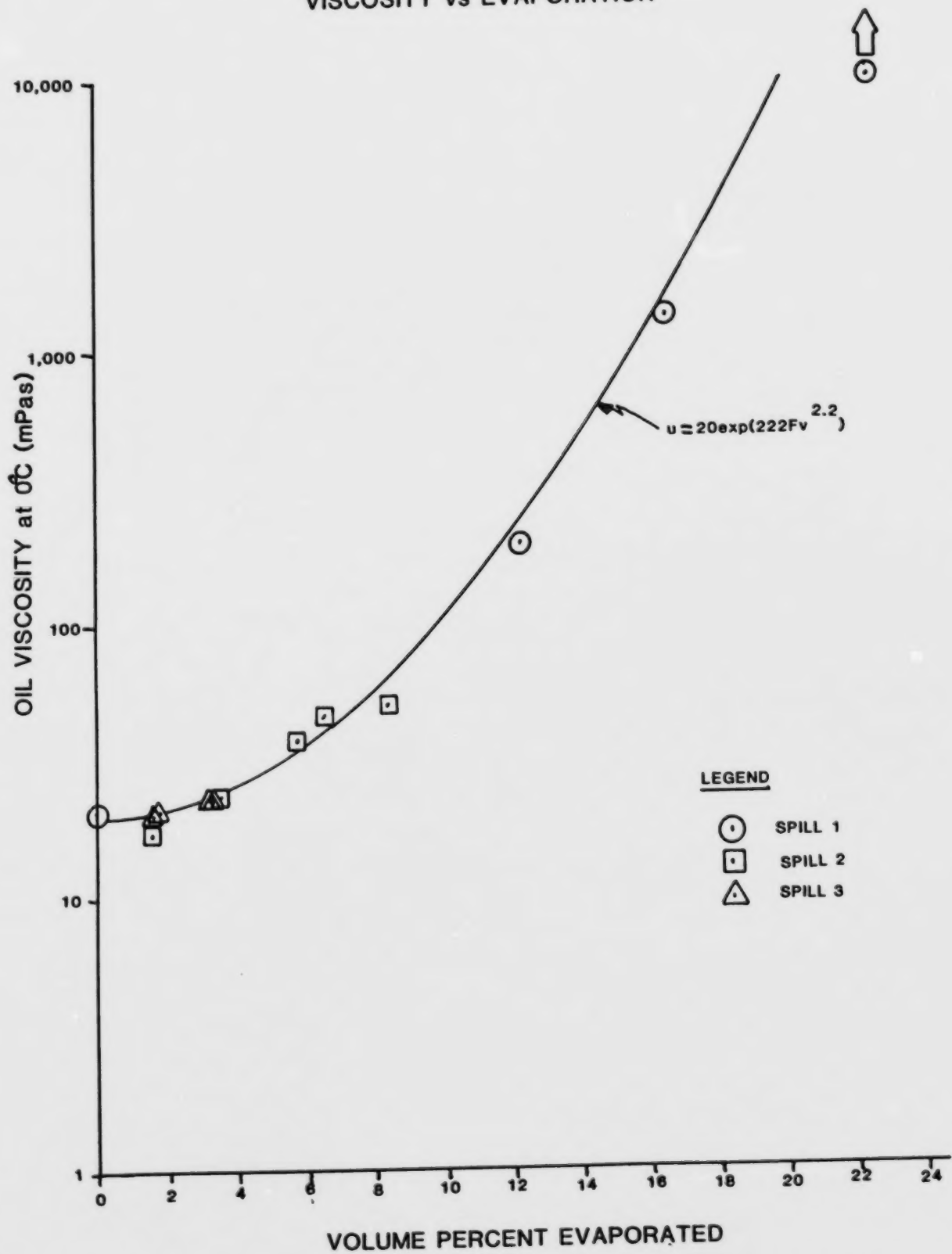


FIGURE 5
VISCOSITY vs EVAPORATION



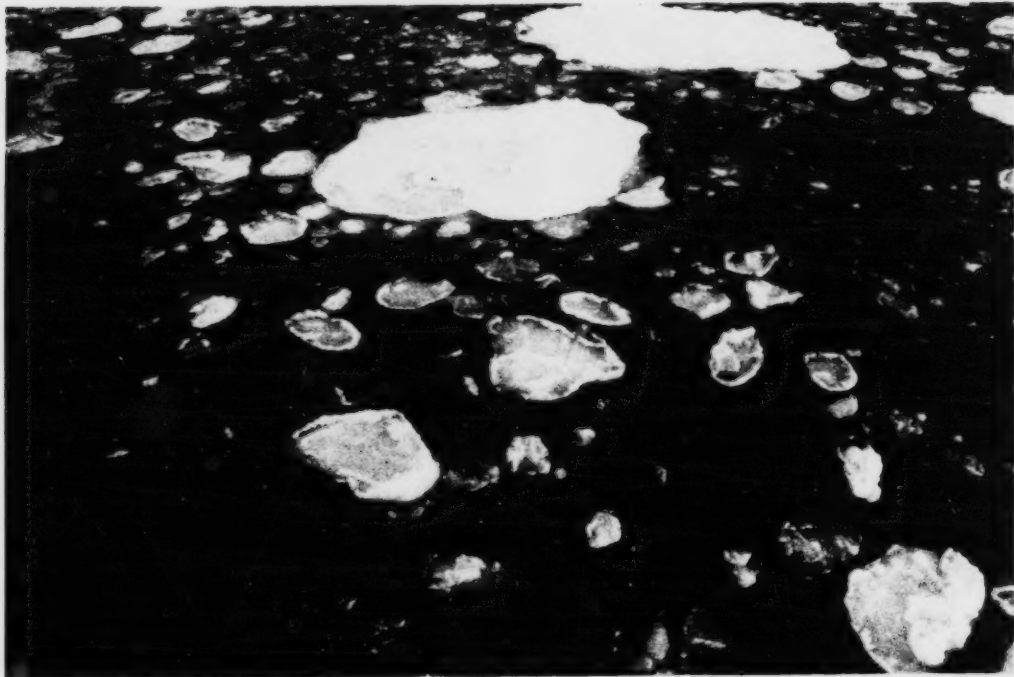


PLATE 10 - OIL FROM SPILL ONE AFTER THREE HOURS (NEAR CENTRE)



PLATE 11 - OIL ON SMALL PANCAKE AMIDST SHEEN

In-Situ Burning

Since the oil was thick and concentrated at the end of spills 2 and 3 it was ignited with a burning, oil-soaked sorbent pad (Plates 12 and 13). The burns lasted about 20 minutes each and probably consumed about 80% of the oil. Further analysis of the data will refine these combustion efficiencies. Table 3 shows the preliminary mass balance for each spill.

Samples of the oil, soot and burn residue were subjected to extensive analyses by the EPS Analytical Services Division to determine levels of the 25 polycyclic aromatic hydrocarbons (PAH's) on the U.S. EPA priority list. The fresh crude oil contained 440 ug/g total PAH's, the two burn residue samples contained 190 and 510 ug/g total PAH's and the soot contained 420 ug/g total PAH's. No significant difference is evident.

TABLE 3
PRELIMINARY OIL MASS BALANCE

SPILL NUMBER	OIL RELEASED (m ³)	EVAPORATED	VOLUME OF OIL BURNED	RECOVERED	TOTAL
1	1	25% of thick 30++% of thin	0	0	25+%
2	1	5%	77%	5%	87%
3	1	4%	80%	0	84%

SUMMARY

Although only preliminary, the results of the field spills indicate that:

- 1) evaporation and subsequent property changes for spills of oil in pack ice can be accurately predicted
- 2) spreading of oil in pack ice is dramatically slower than in open water and that brash ice concentrations seem to be the determining factor
- 3) emulsification and dispersion do not seem to play as important a role in determining the fate of a spill in pack ice as they do for spills on open water
- 4) in-situ burning is an effective countermeasure for oil spills in high pack ice concentrations.

ACKNOWLEDGEMENTS

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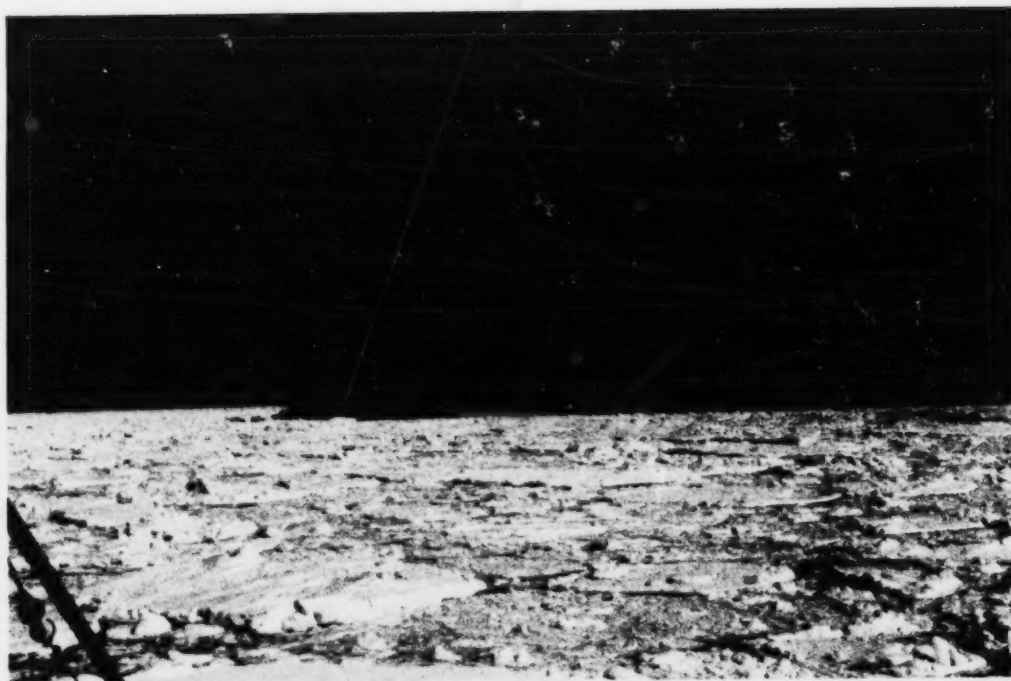


PLATE 12 - BURNING SPILL 2



PLATE 13 - BURNING
SPILL 3

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THE ALASKA CLEAN SEAS RESEARCH, DEVELOPMENT AND ENGINEERING PROGRAM

Richard V. Shafer, P.E.
Alaska Clean Seas

INTRODUCTION

A chief objective of the Alaska Clean Seas organization has been, from its early beginnings in 1978, to advance the state of the art for oil spill response in arctic waters. Alaska Clean Seas--originally known as ABSORB, an acronym for Alaskan Beaufort Sea Oil Spill Response Body--was formed by oil companies with interests in the 1979 joint federal-state offshore lease sale off the northern Alaskan coast. Among the organization's purposes was--and still is--a commitment ". . . to an efficient and effective cleanup organization, . . ." and ". . . to investigate and acquire appropriate equipment and materials, and to develop training programs for personnel who will be involved in the cleanup of oil spills . . ." (*Articles of Agreement for Alaska Clean Seas*, 1985)

EARLY RESEARCH, DEVELOPMENT AND ENGINEERING PROGRAM

The ARCAT Design

A significant example of ABSORB's early research, development and engineering efforts is the ARCAT design development. Member companies recognized the need for a skimming vessel which could operate in the broken ice and open water environments found in the Beaufort Sea area during summer and fall months. Analysis of the first design effort, the ARCAT I design, revealed potential stability problems and somewhat limited range of operating capabilities. A redesign effort benefited from the earlier experience and produced a 20-m catamaran design with improved stability and enhanced capability. This vessel, The ARCAT II, which has twin hulls specially designed to resist ice forces, is deployed at Prudhoe Bay where it is the keystone of Alaska Clean Seas' Beaufort response system. (Williams, 1982)

Other Early Research, Development and Engineering Work

Other research, development and engineering projects are listed below: (Hillman and Shafer, 1983; Hillman, 1985)

- o Experiments involving oil in ice. (Nelson and Allen, 1982)
- o Experiments in shaping the under surface of ice by varying the insulating value of materials at the surface. (Nelson and Allen, 1982)
- o Coastal resource manuals for the Beaufort Sea (Morson, et al., 1983.) and the Bering Sea (under preparation) each with a section covering spill response considerations.
- o A critical review of resource documents published by others for Bering Sea areas.
- o Spill trajectory models for both the Beaufort and Bering Sea areas.
- o Investigations on the effectiveness of dispersants in cold water.
- o Research on the use of air cushion vehicles for logistic support.

- o Contribution to Canadian research on fireproof boom and air deployable igniters.
- o Flare burner experiments.
- o Oily refuse incineration research.
- o Transfer and storage system evaluation.
- o Development support for the Moorhead beach cleaning device.
- o Field and laboratory testing of three deep-draft containment booms.

The area of interest of the organization has now expanded to include additional areas in the Beaufort the Bering Seas, and potentially other waters surrounding Alaska could be included as well; and the name has been changed to Alaska Clean Seas, reflecting the organization's broadened responsibilities. Figure (1) depicts the organization's present organizational structure.

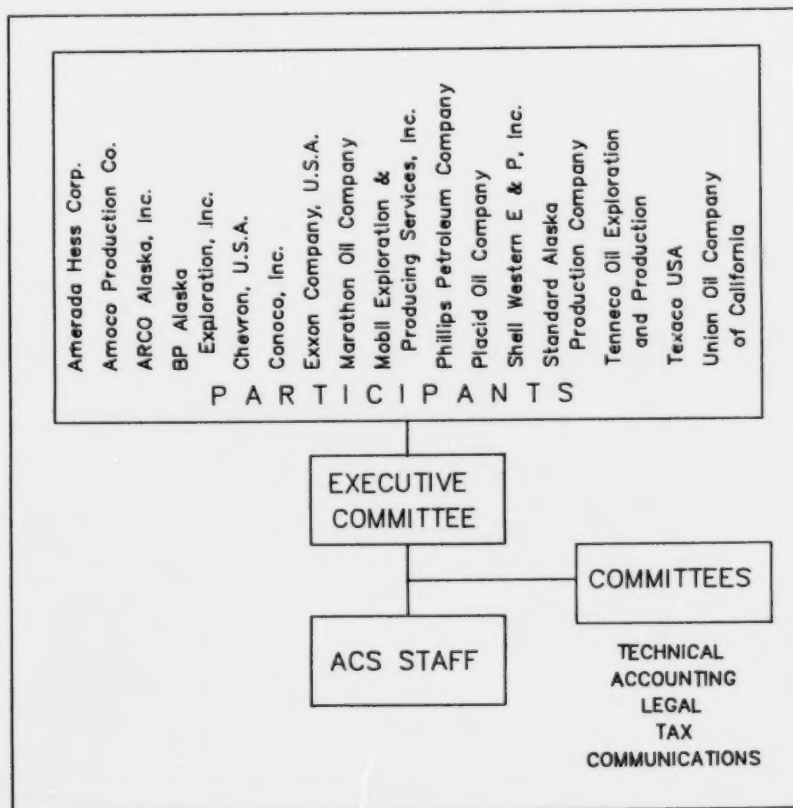


Figure 1. Alaska Clean Seas organization.

THE 1985 RESEARCH PROGRAM

Listed and discussed in the following paragraphs are research and development projects undertaken by Alaska Clean Seas during 1985.

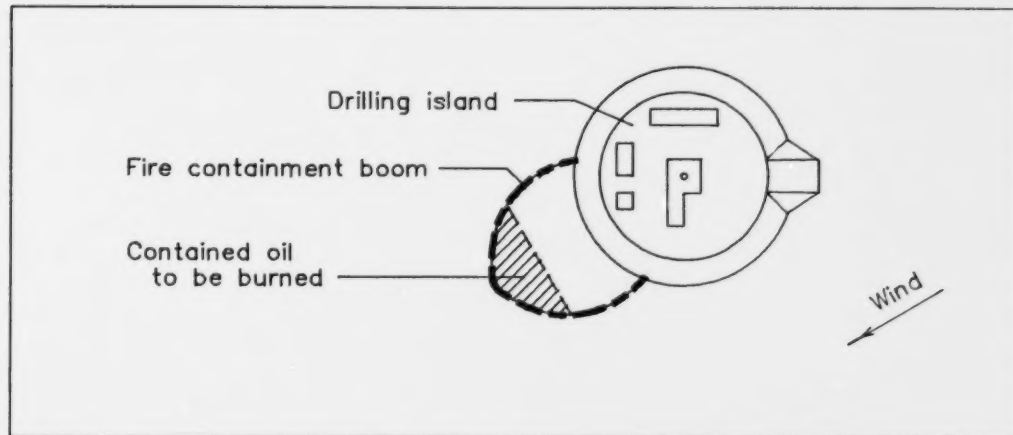


Figure 2. Deployment of fire containment boom downwind of drilling island.

Fire Containment Boom Assessment

Various firms have developed designs for special containment boom which is resistant to damage by fire. Such boom can be used to facilitate disposal of spilled oil by *in situ* burning. Fire containment boom must be

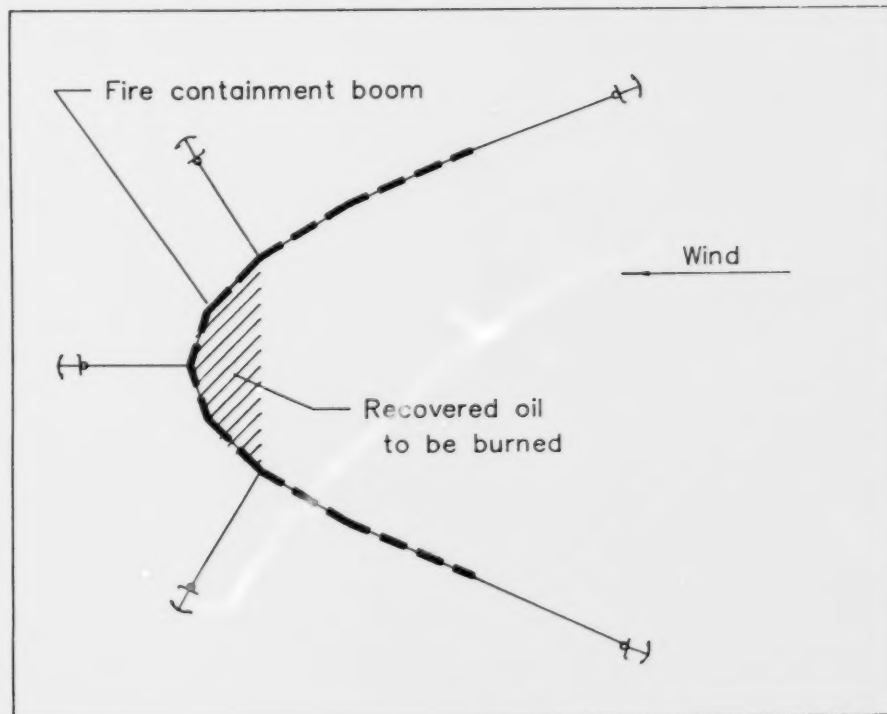


Figure 3. Deployment of fire containment boom in open water.

designed to provide for containment of spilled oil in a layer sufficiently thick to support combustion while resisting the effects of heat well enough to functionally survive exposure to the burning oil.

This project was conducted to assess survivability, containment capability, and other characteristics of various designs and configurations of fire containment boom. (*Test and Evaluation of Fire Containment Boom*, 1986.) In all, 7 burn tests were performed. They demonstrated that several boom types are available which will functionally survive a 24-hour exposure to burning oil. Figures 2 through 4 illustrate some of the possible variations in deployment of fire containment boom.

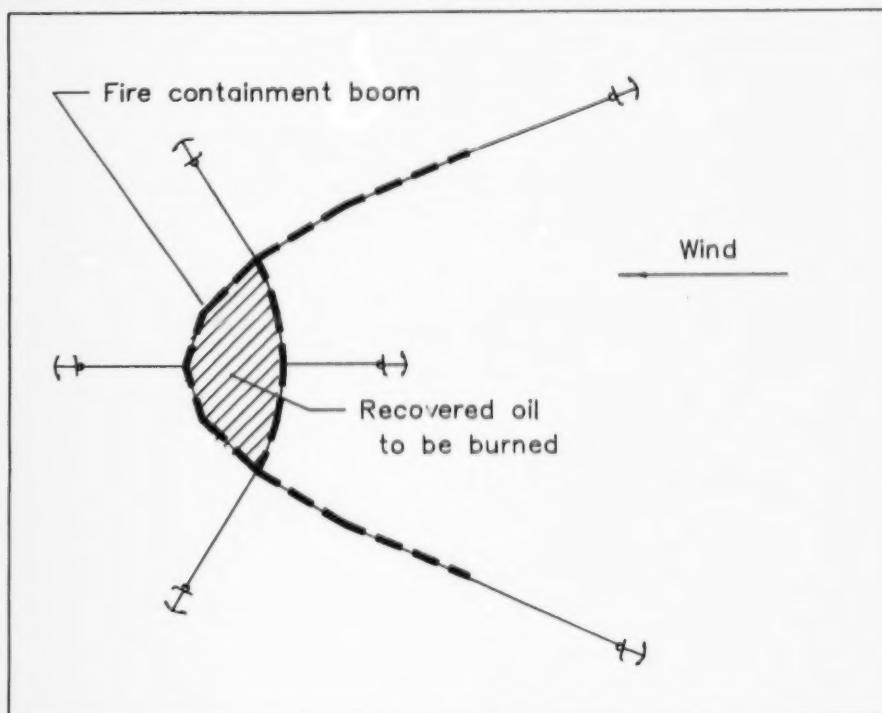


Figure 4. Deployment of additional fire containment boom will increase burn volumes.

Bubble Barrier

If air bubbles are injected into the water column at some depth beneath the surface, the resulting water mass containing bubbles, being less dense than water alone, will tend to be buoyed up by the surrounding water. Anything floating on the surface, such as oil, will tend to be pushed away from the area of the bubbles, (1) because the surface over the bubbly area will be elevated somewhat above the surrounding water surface, and (2) because surface currents will be set up which flow away from the bubbly area. A bubble barrier should provide good fire containment, as shown in Figure 5. A submerged bubble barrier should be successful in containing oil while allowing large blocks of ice to move freely past, as shown in Figure 6.

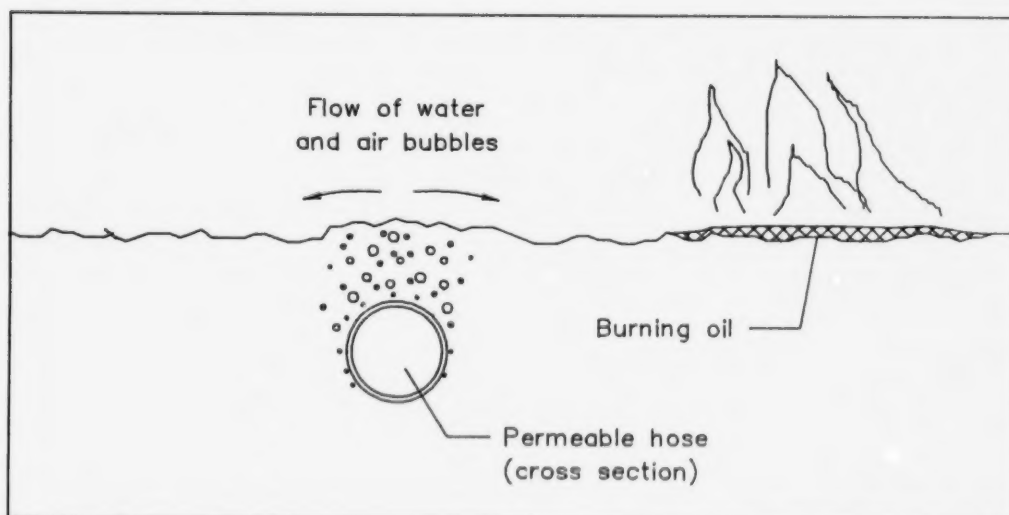


Figure 5. Near-surface bubble barrier.

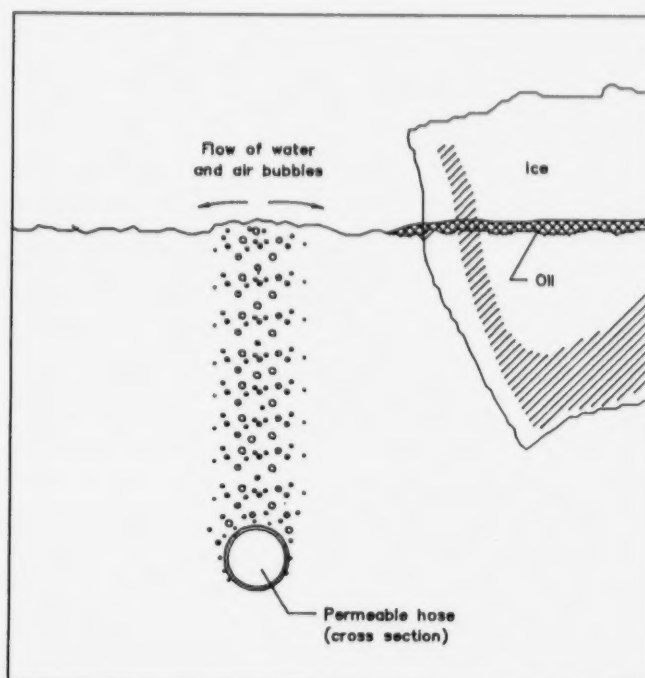


Figure 6. Submerged bubble barrier. Ice blocks should pass freely but oil will be expected to be contained.

This project was designed to study (1) variations in behavior of bubble barriers with depth, (2) the spill containment capability of the barrier in the presence of broken ice, and (3) the feasibility of using bubble barrier

systems for spill containment in arctic waters. Results of the ongoing Alaska Clean Seas bubble barrier design development and testing program include the following observations:

- o A prototype bubble barrier system was found to be more easily maneuvered in water than conventional boom because of the bubble barrier's smaller cross-section.
- o Under one-foot harbor chop and 15-knot wind conditions a prototype bubble barrier was able to hold back cotton seed hulls (simulating an oil slick) at a distance of 2 to 3 m. In addition, it was noted that a water current of approximately 1/2 knot did not adversely affect the bubble plume.

Additional tests were conducted earlier this year involving oil and ice in the Esso Resources, Canada test tank. Field tests are planned to be conducted in the Prudhoe Bay area during summer, 1986.

Enhanced ARCAT Recovery (Plunging Water-Jet Boom)

A jet of water directed down into the surface of the water will tend to entrain air and inject it into the upper part of the water column. The injected air will make the affected water buoyant relative to surrounding water, and it's surface will be higher thus creating a barrier to movement of oil on the surface. See Figure 7.

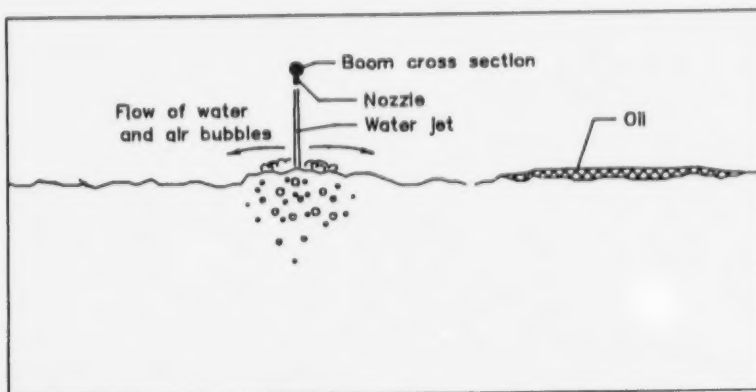


Figure 7. Water jet boom.

Conceptually, a system of water jets arranged in a "V" configuration ahead of the ARCAT skimming vessel should enhance its skimming capability by providing a greater swath width. The water jets should also help rinse oil off floating ice in the area covered by the jets. This project was designed to assess different jet designs and configurations and provide a guide for the design of water jet booms. The prototype jet booms have been fabricated from stainless steel. Their performance has been evaluated in a test tank. Subsequent full scale tests will be performed in Galveston Bay before the equipment is mounted on the ARCAT for field testing and operational purposes during summer, 1986.

Air Deployable Igniters

Alaska Clean Seas has in stock a sizeable inventory of air deployable igniters. These devices were developed by Canadian operators (with some

financial support from Alaska Clean Seas) as a device to help initiate *in situ* combustion of spilled oil. Such igniters would ordinarily be applied to a spill area by dropping them by hand from a helicopter. This is illustrated in Figure 8.

While igniters of the type now stocked by Alaska Clean Seas have been demonstrated to be effective, a number of improvements are desirable. The objectives of this project, (*Survey and Analysis of Air Deployable Igniters*, 1986.) are to review available information on alternative igniter designs, seeking a design with smaller size and weight, improved performance in thin or weathered oils, greater simplicity of use, and lower cost. Project scope includes review and analysis of existing design details and

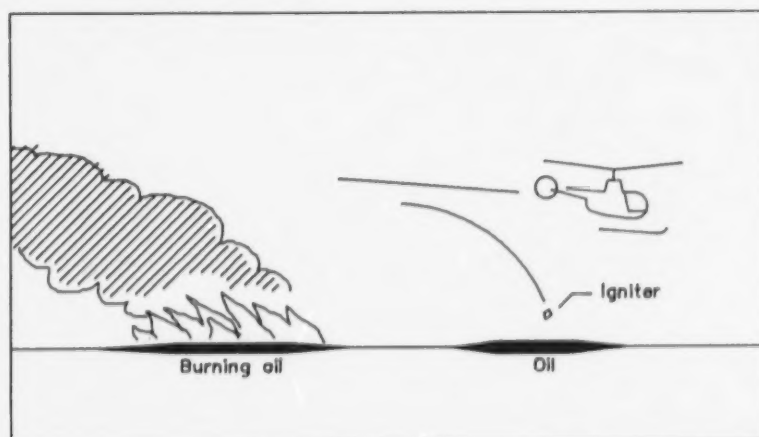


Figure 8. *In situ* combustion using air-deployed igniters.

problems, examination of ignition promoters, investigation of mechanisms to minimize splash effects, and proposal of new igniter concepts if applicable.

The study evaluates 5 devices. They are listed and discussed below.

- (1) Pyroid "Sandwich" Device. Development of this device was sponsored by the Canadian Environmental Protection Service. It uses a solid rocket fuel sandwiched between two polystyrene blocks.
- (2) Dome "Tin Can" Igniter. This is the same type of device which is presently stocked by Alaska Clean Seas. It includes a fuse and a small quantity of solid propellant which, when activated, ignites a charge of gelled kerosene. The device employs a pair of juice can sized floats.
- (3) Laser Igniter. Under development in Canada is a system for ignition of oil using a combination of laser beams to first heat the oil to help volatilize it and then to ignite it. Static tests of the device look promising.
- (4) "Helitorch" Device. This equipment, which has been used in combating forest fires, uses a device slung beneath a helicopter to ignite gelled hydrocarbon fuel as it is released onto the target. This system appears to be a feasible alternative to presently employed igniters.
- (5) Premo "Aerial Ignition Device" (AID). This system involves ejecting small polystyrene balls filled with substances which

produce delayed ignition. Specifically, the hollow balls are filled with potassium permanganate. They are injected with ethylene glycol at the time they are ejected from the helicopter. The two chemicals produce an exothermic reaction which results in ignition after a few seconds.

The results of this study will provide the basis for decisions regarding further igniter research and development work.

Oil Spill Chemical Application Manual

A substantial amount of information is available regarding the use of dispersants and other spill response chemicals in the arctic. This information is not, however, in a form readily available for spill response planners or those who must direct spill response operations in an emergency. This project synthesizes available information on spill response chemicals and various related environmental and logistics data into a single oil spill chemical application manual for use by response planners and managers. (*Alaska Oil Spill Chemical Application Manual*, 1986.)

Logistics Support for U. S. Coast Guard Spill Trajectory Study

In addition to the research and development projects with which Alaska Clean Seas was directly involved in 1985, substantial logistics support was provided to the U. S. Coast Guard during the course of field work on a spill trajectory study. Alaska Clean Seas and member companies provided vessels and crews plus office space and living quarters for the Coast Guard personnel to use while acquiring data for the study.

THE 1986 RESEARCH AND DEVELOPMENT PROGRAM

Alaska Clean Seas is undertaking the following projects in 1986:

Shoreline Protection Using Porous Netting

Perhaps the most serious risk of biological damage from an oil spill is associated with affected shorelines. When an oil spill impacts a beach, the cleanup methods commonly used are either very labor intensive or they remove a great deal of soil along with the oil. And they are invariably quite costly. Conventional beach cleanup techniques are relatively slow, especially in remote areas; and the longer oil remains on a beach or in wildlife habitat, the greater the potential for biological damage.

This project assesses the concept of placing a thin, lightweight, fine mesh material on a threatened shoreline. Long sheets of this netting would be applied at or near the next expected high tide elevation where most of the oil would be deposited. It could be delivered to remote shorelines by helicopter and quickly deployed by a small number of workers. Figure 9 illustrates how such material might be deployed.

When oil or oily emulsion is deposited on the shoreline it will settle on top of the porous mesh. The surface characteristics of the mesh must be designed to allow water to percolate through the fabric into the soil but to retain oil. On a receding tide, the mesh fabric could be rolled up, thereby capturing virtually all of the oil or emulsion but not robbing any substantial quantity of beach material. The rolled up fabric would then be disposed of in an approved manner.

This project will involve the following steps:

- (a) Manufacturers of plastic netting, sheeting and fabrics will be contacted to see if they can produce a very lightweight, inexpensive netting with appropriate characteristics.
- (b) Samples of various prospective material formulations and designs will be purchased and applied to natural and artificial shorelines where recovery effectiveness and efficiency will be assessed. Integrity of the oleophilic material under cold conditions will be considered in its design and testing, and designs will seek to minimize problems with wildlife entanglement.
- (c) Deployment and anchoring methods will be developed and assessed. Field tests are planned for the Alaskan arctic during summer, 1986.

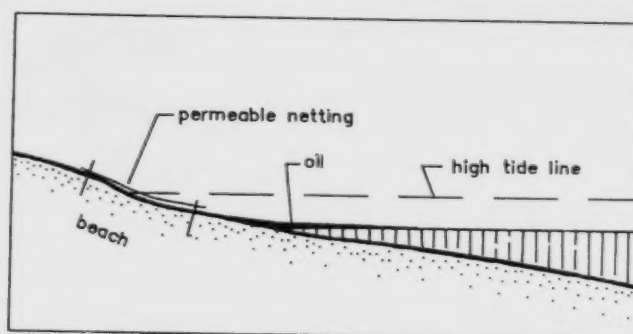


Figure 9. Shoreline and habitat protection using permeable netting.

Refinement of Aerial Ignition System

As discussed earlier, present methods for igniting spilled oil for *in situ* disposal are effective but involve some risk to personnel and equipment. The objective of this project are: (a) identification or development of oil ignition systems which do not involve a spark or open flame onboard the deployment platform (i.e., fixed wing aircraft or helicopter), (b) reduction of splash effects upon impact, (c) maximization of flame contacting area with the oil, and (d) minimization of costs.

As mentioned elsewhere, the 1985 Alaska Clean Seas project, Survey and Analysis of Air Deployable Igniters, identified the strengths and weaknesses of the following ignition systems:

- (a) Dome/Energetex "Tin Can" igniter,
- (b) EPS Pyroid igniter,
- (c) EPS (Arctec/PSI) laser igniter,
- (d) Helitorch igniter, and
- (e) Premo "Ping-Pong Ball" Aerial Ignition Device.

None of these existing systems presently satisfies all of the Alaska Clean Seas objectives for a safe, reliable, and efficient igniter at a reasonable cost. Some of these systems do, however, offer significant potential as components of or as a source of ideas for the development and field testing of new ignition devices.

This project will involve:

- (a) Development and testing of innovative ignition systems for burning oil *in situ*.
- (b) Initial field testing of selected concepts under various igniter configurations, drop heights, oil film thicknesses, and wind conditions.
- (c) Larger scale tests of most promising designs using helicopters to deploy ignition devices into a larger test tank or pond.

Dispersant Effectiveness Test in Cold Water Conditions

Laboratory work conducted in 1980 demonstrated that the dispersant chemicals presently stockpiled by Alaska Clean Seas are effective for use on Prudhoe Bay crude oil under arctic conditions. However, larger scale tests conducted in a wave basin would provide more realistic test conditions and provide a better basis for recommending procedures and practices to be included in the *Alaska Oil Spill Chemical Applications Manual* recently published by Alaska Clean Seas. (See references.) Furthermore, since 1980 additional dispersants have been developed that are expected to be more effective in cold water applications, and these new chemicals can be assessed.

This project will involve the following steps:

- (a) Selection by the Alaska Clean Seas Dispersant Subcommittee of two or more dispersants to be tested. Selection will be based on information gathered for the *Alaska Oil Spill Chemical Applications Manual* and discussions among industry persons working in the oil spill chemicals field.
- (b) Testing of dispersability of Prudhoe Bay crude under controlled wave and temperature conditions at the Esso Resources Canada wave basin in Calgary, Canada. Data collected will include dispersion effectiveness based on fluorometric information, oil droplet size and visual observations with 35-mm still camera and color video camera.

Detection of Oil Under Ice by Induced Fluorescence

There are presently no efficient and effective methods for detecting the presence of oil encapsulated within the sea ice or trapped beneath it. One promising approach to detection of such oil involves use of induced fluorescence.

Crude oil fluoresces strongly in the visible spectrum when it is illuminated with ultraviolet light. Conceptually, as shown in Figure 10, a compact, portable, pulsed ultraviolet light source, similar to a photographic strobe light, might be used to flash an intense beam of ultraviolet light onto a small area of the surface of the sea ice. The light would need to be sufficiently intense to penetrate several feet of snow cover and ice, and illuminate an underlying layer of oil. Oil absorbs ultraviolet light and fluoresces strongly at a much longer wave length in the visible spectrum. A sensor mounted adjacent to the ultraviolet light source should detect fluorescence from any oil present.

This project will involve the following steps:

- (a) Manufacturers of photographic strobe equipment and commercial ultraviolet sources will be contacted to design and fabricate a 1-2 KW sec ultraviolet flash tube and power supply.

- (b) Samples of Prudhoe Bay crude oil will be placed under preserved samples of Beaufort Sea ice and snow and subjected to illumination from selected ultraviolet sources. The intensity of the return fluorescence will be measured. Factors to be investigated are intensity and spectral purity of the light source, optimum band-pass width of commercially available optical filters, sensitivity and response time of commercially available photo detectors, and conversion efficiency and decay time of the fluorescence process.
- (c) Development and testing of a "breadboard" prototype device.
- (d) Depending on the success of tests conducted with the breadboard prototype, further work might be done toward design and fabrication of a unit for practical use in the field.

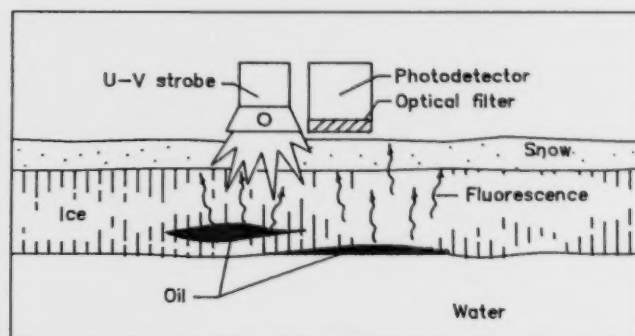


Figure 10. Through-ice oil detection system concept.

Multiple boom Strategies for Use in Arctic Waters

Virtually all booms exhibit exponentially increasing oil underflow losses when the local normal flow velocity exceeds 1 to 1.5 knots. In the presence of waves, underflow begins at lower velocities, and wind-driven choppy waves can also cause oil to splash over booms, particularly low profile booms such as the more massive fire resistant booms. Short-period waves also inhibit the ignition and subsequent incineration of oil, significantly reducing the effectiveness of the *in situ* burning disposal technique. In arctic waters the additional possibility of collision with moving ice threatens the structural integrity of the booms.

A promising concept for extending the use of booms into these more severe conditions involves use of multiple boom arrays. The concept utilizes a configuration of perforated or other specially designed booms upstream of the final boom to establish a quiescent containment region, isolated from choppy waves and high currents. In this region, the thick, relatively stagnant pool of trapped oil will burn efficiently. See Figure 11. Multiple booms have also been proposed for ice containment and diversion.

The proposed project will involve:

- (a) measurement of environmental loads and comparison of different controlled failure mechanisms for upstream boom elements,

- (b) exploration of other design issues such as the number, size and spacing of boom units; and
- (c) the establishment of deployment guidelines.

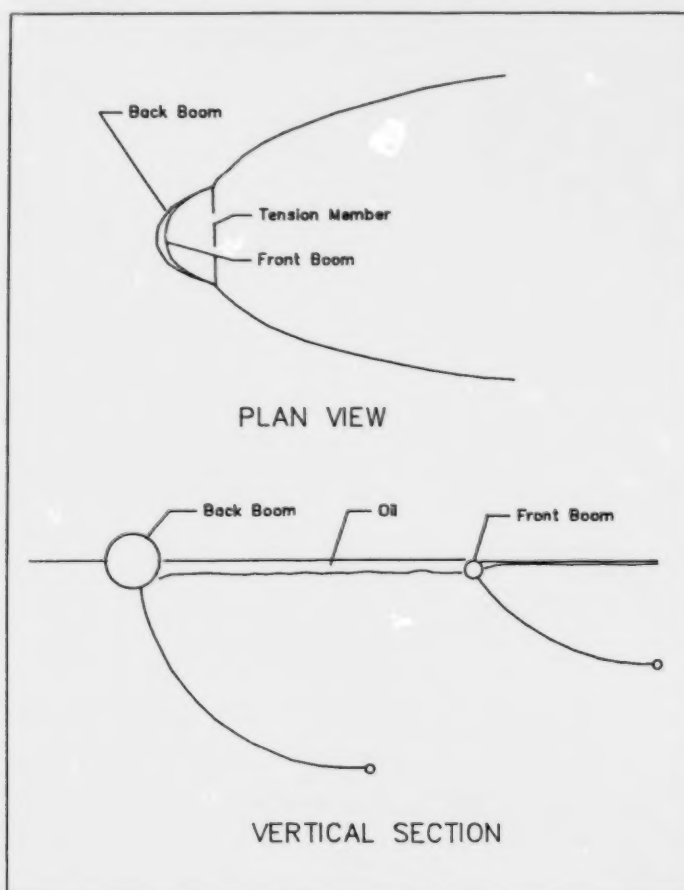


Figure 11. Typical multi-boom configuration.

CONCLUSION

The Alaska Clean Seas research and development program continues to help advance the state-of-the-art for oil spill response in arctic waters. Knowledge gained through this ongoing program is used to update contingency planning manuals and the ACS training curriculum to help member companies maintain and improve the quality and effectiveness of their spill countermeasures.

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THE COMPLEX PERMITTIVITY OF CRUDE OIL

by

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INTRODUCTION:

The detection of oil under sea ice using radar methods is difficult because of the absorption of the electromagnetic waves in the ice. The waves cannot penetrate a few metres of typical first year ice at frequencies greater than 1GHz, say. As a result, signals from oil at the ice-water interface are likely to be strongly masked by scattering from the upper surface and from inclusions in the body of the ice, such as air bubbles and brine drainage channels. Detection of oil, which is basically a problem of classifying radar signals, is likely to be frustrated by the high effective noise levels. Thus it is prudent to look for those properties of oil which may highlight its presence by providing significantly greater information to the classifier. This could be in the form of measurements at different frequencies.

There is some evidence, provided by measurements of Dean (1984), to suggest that crude oil may exhibit an enhanced absorption at a frequency near to 1GHz. The purpose of this study is to look carefully at Norman Wells crude for anomalous absorption in the range 100 MHz to well above 1 GHz. In fact, the performance characteristics of our equipment are responsible for the upper limit of 1.5 GHz. The method involves similar equipment to that used by Vant et al (1978) in their measurement of the dielectric properties of sea ice. However, Vant et al employed a transmission method in contrast with the present work which utilises a reflection technique. The complex dielectric constant is computed from the measurements so that, if present, the anomalous absorption can be determined.

METHOD:

A diagram of the equipment is shown in figure 1. The rf signal can be generated either by a swept frequency oscillator or by a frequency synthesizer producing a cw signal. A Hewlett-Packard HP-8690B swept frequency oscillator is employed to examine the general nature of the dielectric properties over a continuous frequency range, whilst for spot measurements a AILTEC 380 synthesizer is used. To find the amplitude and phase of a signal in relation to a reference, the signals are down converted to a few hundred kHz by a HP-3411A Harmonic Frequency Converter and the complex amplitude displayed on a HP-8410A Network Analyser.

The signal from the generator is split into two parts by a power splitter. One output forms the reference signal for the phase determination and is fed to the Frequency Converter. A transmission line of variable length is inserted into this branch so that the relative phase of the reference signal can be adjusted

for calibration purposes.

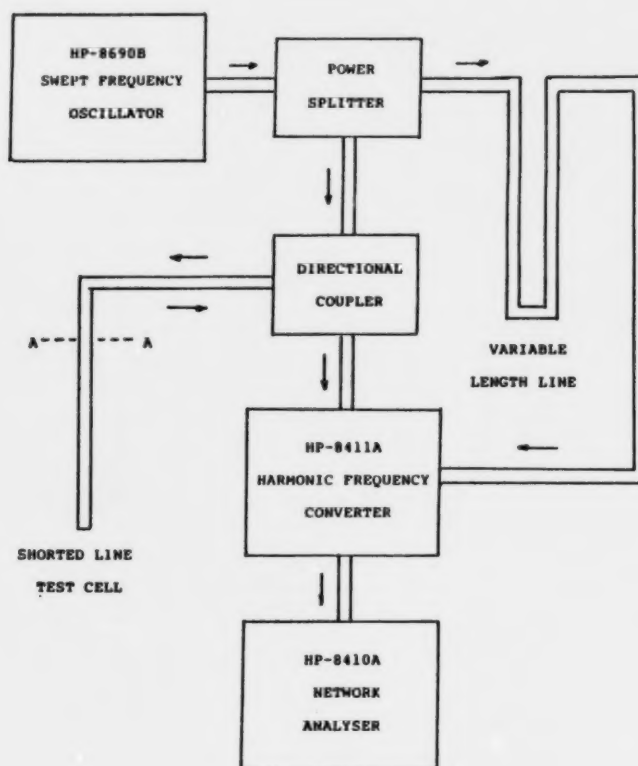


Figure 1
Block diagram of equipment

The other signal from the power splitter is fed to a directional coupler, which provides a signal to a shorted line which acts as a test cell for the crude oil. Reflected power from this cell is fed back through the directional coupler as the test signal to the Frequency Converter. The characteristic impedance of all lines (except the test cell) is 50 Ohm.

The system is calibrated by disconnecting the test cell at point "A" in figure 1 and connecting standard terminations, such as 50 Ohm, short and open circuits. Other terminations, such as 25 or 100 Ohm, can be used as a further check. The variable line can be adjusted, as well as phase and amplitude controls on the Network Analyser, to bring the spot on the CRT to the appropriate positions on a Smith chart overlying the screen. Thus the impedance of the test cell can be read off by reconnecting it to point "A". The calibration is only valid over a limited frequency range of a few tens of

MHz. Therefore the swept frequency mode can only be used to scan a frequency range for anomalous behaviour; the frequency synthesizer, which includes a digital readout should be employed for actual measurements of impedance. These are then converted to complex dielectric constant.

The test cell is a shorted coaxial transmission line that can be filled with oil. It is constructed of copper with a standard 1/4 inch rod forming the inner conductor and a standard tube with inner diameter 0.55 inch forming the outer. The short comprises a copper plate, soldered on one end, whilst a General Radio connector is soldered on to the other end. The central rod is tapped so that the inner conductor of the GR connector can be screwed into it and the plastic spacer in the GR connector is kept to centralise the rod and inner conductor of the connector. A diagram of the cell is shown in figure 2.

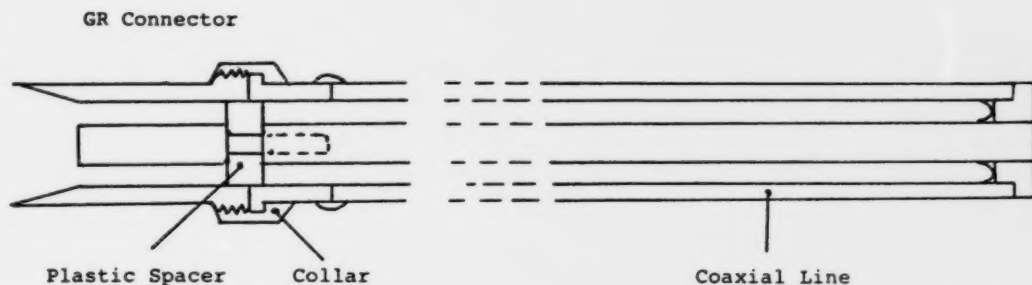


Figure 2
Diagram of test cell transmission line

The dimensions of the cell are chosen so that its characteristic impedance with air dielectric is close to that of the system and so that oil with a viscosity of a few hundred centipoise can easily be poured into it. For a coaxial line, the characteristic impedance with air dielectric is given by Bleaney and Bleaney (1959):

$$Z_0 = (2\pi)^{-1} (\mu_0 / \epsilon_0) \ln(b/a)$$

where a and b are the diameters (outer and inner) of the inner and outer conductors respectively. It is soon verified that, if Z is measured in Ohms:

$$Z_0 = 60 \ln(b/a).$$

For the above dimensions we calculate the characteristic impedance of the cell to be 47.3 Ohm. However, this assumes that the system is perfectly aligned: because the rod is likely to be slightly off-centre and closer to the wall, it

can be expected that the actual value is a little less than this.

Standard transmission line theory (Bleaney and Bleaney, 1959) or reference to Scaife (1971) shows that the impedance of a shorted line is given by

$$Z_A = iZ_0 \tan(2\pi L n / \lambda) / n$$

where L is the length of the line, λ is the wavelength in air and n is the complex refractive index, which is related to the complex relative permittivity by

$$n = \epsilon^{1/2}$$

By writing

$$\gamma = 2\pi i n / \lambda$$

this can be put into the form:

$$Z_A = (2\pi i Z_0 L / \lambda) \tanh(\gamma L) / (\gamma L)$$

where, if

$$\gamma = \alpha + i\beta,$$

the real and imaginary parts of the dielectric constant are

$$\epsilon' = (\lambda / 2\pi)^2 (\beta^2 - \alpha^2)$$

$$\epsilon'' = (\lambda / 2\pi)^2 2\alpha\beta,$$

respectively. The real part is related to the wavelength of the waves on the line whilst the imaginary part represents the loss. To find a solution for complex ϵ , given Z_A , it is necessary to solve a transcendental equation of the form

$$\tanh z - kz = 0$$

where k is a complex constant. By considering just imaginary z and k , it is clear that, because the tangent is periodic, there are many solutions and it is necessary to specify the domain in which the solution lies. When k is complex this is still true and is equivalent to knowing the approximate electrical length of the line ahead of time. The solution is conveniently accomplished numerically by Newton's method (the method is described by Shoup, 1979) but extended to the complex plane. However, it is well-known that Newton's method is apt to diverge and in fact this was observed in early versions of the program: the domain of convergence was not sufficient. Therefore a linear search algorithm is implemented to find a better first trial solution. This is based on the assumption that, to a first approximation, the imaginary part of the dielectric constant is zero. An approximate solution is found which is then used as a trial input to the Newton algorithm; in general a complex solution is returned. The resulting program provides satisfactory results

except when the length of the line is such that the impedance is very high. In this case the length is close to a multiple of a quarter wavelength and a hand calculation could give adequate results. The program has been tested extensively by coding another program to generate input data from a given complex dielectric constant.

A sample run of the program is shown in figure 3.

```

do you need to create a parameter file (y/n)
n
length of cell 0.5900 m
characteristic impedance 45.00 ohm
enter frequency (MHz)
1200
number of free space quarter wavelengths 9.4
enter number of quarter wavelengths expected
14
enter real part of  $z_0$  (ohm)
3.5
enter imaginary part of  $z_0$  (ohm)
8

real permittivity 2.25
imag permittivity -0.02

```

Figure 3
Sample run of program

RESULTS:

Two transmission line test cells were employed. The first was approximately 0.59 m in length and the second about 0.15 m. The exact electrical lengths and characteristic impedances were not known in advance and were estimated by taking measurements with air as the dielectric. These parameters were found by entering trial parameters and the data into the program and adjusting the parameters until the real part of the dielectric constant was unity and the imaginary part zero. This condition was satisfied for several spot frequencies in the chosen frequency range. The results of this are shown in Tables 1 and 2.

TABLE 1

CALIBRATION FOR LONGER LINE

Length of Line: 0.59 m
 Characteristic Impedance: 45 Ohm

Frequency (MHz)	Real Z (Ohm) ^A	Imag Z (Ohm) ^A	Real ϵ	Imag ϵ
200	0.0	-36	1.00	0.0
400	0.0	-175	1.01	0.0
600	0.0	95	1.00	0.0
800	0.0	135	1.01	0.0
1200	0.0	-36	1.03	0.0

TABLE 2

CALIBRATION FOR SHORTER LINE

Length of Line: 0.158 m
 Characteristic Impedance: 45 Ohm

Frequency (MHz)	Real Z (Ohm) ^A	Imag Z (Ohm) ^A	Real ϵ	Imag ϵ
500	0.0	-500	1.01	0.0
700	0.0	-50	0.99	0.0
900	0.0	-10	0.97	0.0
1200	0.0	47	0.99	0.0
1800	0.0	-16	1.00	0.0

The electrical length of the longer line was established as 0.590 ± 0.005 m and its characteristic impedance as 45 ± 1 Ohm. The line was filled with oil, supplied by ESSO Resources, and the measurements repeated. Figure 4 shows the results over the range 100 MHz to 1.2 GHz with the longer line data represented by circles: the real part of the dielectric constant is more or less constant with a value of 2.2 and it is possible that there is a small imaginary component at about 0.02. Again the imaginary part, if it really exists, does not appear to be a strong function of frequency. The cyclical structure is felt to be an artefact possibly due to high standing waves in our apparatus. The impedance was also examined in the swept frequency mode: no evidence of narrow absorption lines could be seen.

Calibration data for the shorter line yielded a length of 0.158 ± 0.001 m and a characteristic impedance of 45 ± 1 Ohm. When the shorter line was filled with oil it was found that the real part of the dielectric constant was significantly smaller than that found for the longer line. The effective length of the line was reduced to 0.155 m to achieve a better match with the above results for the longer line. The justification for this lies in the

uncertainty caused by the plastic spacer in the GR connector, which has a width of about 3 mm, and that associated with the finite diameter of the line: with the shorter line, end effects are proportionately greater. With this change the dielectric constant is similar to that derived from the other line. No evidence for anomalous absorption was noted in the swept frequency mode. The data is represented by triangles in figure 4.

Estimates of errors were obtained by varying the input data to the program by an appropriate amount and recalculating the dielectric constant. The results tend to be more accurate for a long line at the higher frequencies. However, when calculating the dielectric constant, the long line is also more subject to ambiguity in its electrical length.

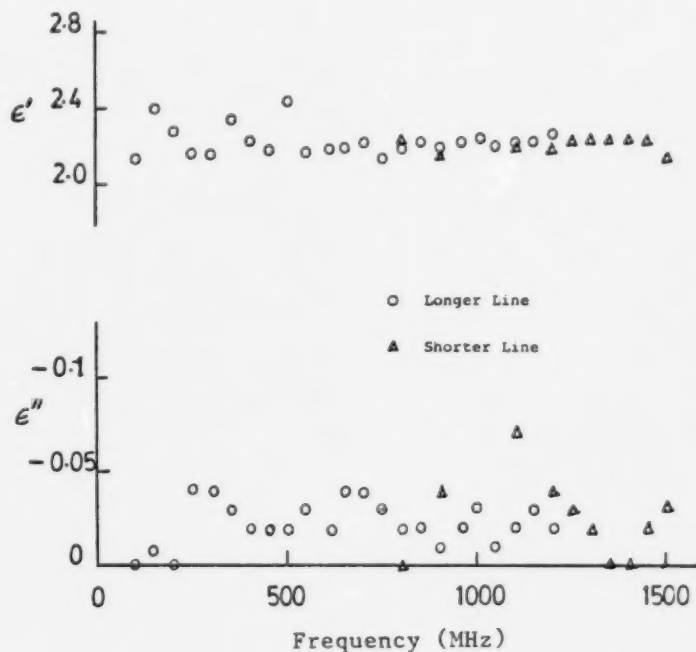


Figure 4
Real and imaginary parts of the dielectric constant

CONCLUSION:

The dielectric constant of our sample of Norman Wells crude oil is 2.2 ± 0.1 over the frequency range 100 MHz to 1.5 GHz; the imaginary part is similarly constant over the same frequency range with a value of 0.02 ± 0.02 . These values are consistent with data for a variety of proprietary petroleum oils assembled by von Hippel (1954): complex permittivities are given for spot frequencies

from 100Hz to 10GHz. Therefore the structure noted by Dean was probably not rooted in the dielectric properties of oil and we cannot rely on any anomalous effects for aiding the detection of oil pollution under sea ice.

In the past, measurements of permittivity have required a compromise between difficulties in the design of the equipment and those involved with the translation of the experimental results into complex permittivity. Our experimental method is particularly direct with the calculations handled by the computer.

ACKNOWLEDGEMENT:

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INSITU MEASUREMENT OF OIL DROPLETS
USING AN IMAGE PROCESSING SYSTEM

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INTRODUCTION

The movement of immiscible fluid droplets is of interest in a large class of problems which includes the dispersion of oil in the presence of wind driven waves. In this situation oil is broken into droplets through the stretching and tearing that accompany the surface wave motion. These droplets are driven down into the water by the turbulent character of the water motion, against the buoyant forces induced by the surrounding water. The forces that compete to control drop motion cause the drops to become segregated. The larger ones, with behavior dominated by buoyant forces, remain close to the water surface while the smaller ones escape this influence and are transported to greater depths. This difference in behavior depends greatly on drop diameter because drop diameter influences both the buoyant force and the drag force that determine drop motion. For this reason the ability to measure drop diameter has great importance in the study of dispersion processes.

Diameters of immiscible fluid droplets have been measured by a number of techniques including those that depend on photographs of the drops insitu. Photographs showing drops in a vertical plane are typical. Some have been obtained by top lighting fluid cells several centimeters thick in the direction of viewing. With this system drop diameters were obtained using a microscope to study the bright spots produced by light reflected off the drop surface (Lin et al.). Another approach has been to backlight small areas of considerable thickness in the fluid space with laser light creating a situation where high powered lenses could function to capture photographs of very small droplets. The backlit-high power lens approach necessitates use of sophisticated image processing systems in order to identify droplets that are not in the plane of interest (Oberdier). The more direct approach using a microscope is extremely tedious and undoubtedly fraught with large potential for error due to eye fatigue if nothing else. Determining characteristics of small regions requires a large number of images to obtain statistically significant information which has led to the use of automated systems that incorporate video recorders coupled with image processors in some instances (Oberdier).

This paper describes a droplet measurement system based on photographs of droplets in the plane of a thin laser sheet and an image processing system that is used to assist in analysis of individual photographs. Diameter and location of oil drops larger than about 0.2mm have been determined with this system.

PHOTOGRAPHIC SYSTEM

Fig. 1 shows the arrangement of photographic components at the measurement section. The laser emits a 3 watt multimode beam made up of light with most of the power at wave lengths of 488 nm and 514.5 nm. The laser transmits a point source light beam under the wind tunnel where it is bent upward and spread into a thin sheet of light. A small mirror bends the beam and a round quartz rod spreads the beam into a sheet approximately 2 mm thick. Oil drops in the tunnel which travel through this light sheet are illuminated and can be photographed. A 35 mm camera and 50 mm normal lens rigidly mounted to the side of the wind tunnel are used to record the images on Kodak Tech Pan film. A gelatin filter attached to the camera lens permits only light which is emitted by the fluorescent properties of the oil drops to reach the film. The result is a photograph characterized by droplet illumination that is highly uniform and essentially free of images or image irregularities produced by reflected light. This includes images produced by debris and irregularities produced by light reflected from the spherical surfaces of the oil drops. A small oil filled capsule mounted to the bottom of the tunnel and illuminated by the laser is recorded on each photograph in order to provide a common reference point for determining the location of individual drops.

The lens system produces an image approximately 1/10 the true size. This has the advantage of increasing the light intensities at the film making short time exposures possible. This is especially important because the light fluoresced by the oil particles is of low intensity.

The resolution of the photographic system is limited by the camera lens which is capable of resolving 63 lines per mm. Single wires as small as 0.03 mm were located and their diameters measured with the photographic system so that in the low oil concentration environment in which the system is employed, image confusion is not expected to contribute to error. Droplets smaller than about 0.2mm cannot be photographed satisfactorily because of the combined influences of low light intensity and droplet motion.

The camera is focused on a grid which is temporarily located in the plane of the laser before each experiment. Photographs of the grid provide the scale ratio required to transform measured drop size to true drop size. Photographs are taken at a shutter speed of 1/125 of a second. This speed is required to stop drop motion in this particular setting. Because of the small amount of time used to photograph the drops and the film's low light sensitivity, large lens openings are also required. In order to have an adequate amount of light, the laser sheet width has to be kept small. The width of the sheet is controlled by the diameter and location of the quartz rod (Fig. 2). A 10 mm rod located below the bottom of the tunnel produces a photograph in which approximately 1/5 of the total area photographed has sufficient light for drop measurement. The region in the tunnel which is photographed is approximately 25 cm wide and 35 cm high.

The total number of drops which appear in any photograph is dependent on the exposure time and the thickness of the laser sheet. Exposure time is kept small so that the motion of a drop is small in comparison to the thickness of the laser sheet and the sample volume is essentially determined by the thickness of the laser sheet.

A standard processing procedure employing HC-110 developer is used to obtain high image contrast on Kodak Tech Pan film.

IMAGE PROCESSING SYSTEM HARDWARE AND USE

The photographs are analyzed by a person with the aid of the interactive image processing system illustrated in Fig. 3. This system uses a TV camera to transform the analog photographic image into a digital format that can be studied to extract information about the drops using the computer that is part of the system.

The negative is sandwiched between a pair of glass plates in a holder. One of the glass plates has a grid etched on the face in contact with the negative that can be used to isolate regions of the negative for analysis. The grid is referred to as the segmenting grid. The holder and negative are placed on a light table and the TV camera is focused on the segment of the negative under study. The TV camera has a standard 25 mm lens and extension bellows for focusing the image on a vidicon tube inside of the camera. This lens is reverse mounted because all analyses have been conducted at high magnification with the lens very close to the negative. A mini-computer on line with the system divides the image into 262,144 separate areas assigning each area, called a "pixel", a light intensity value that represents an average over its area. The light intensity value is an 8 bit real number in the range from -1.0 to +1.0 which produces a black and white image with 128 shades of grey ranging from white to black. The pixels are arranged in a 512 x 512 matrix which makes up the image. The size of a single pixel is one feature of the system that limits the systems capability to determine droplet diameter accurately. Fig. 4 shows the relationship between the camera lens, the TV lens, and the vidicon tube and how each influences the area covered by a single pixel. Drops with diameters less than 4 pixels were eliminated from the data because the potential error in diameter was too large. The digital information characterizing the image is stored in a buffer for processing.

To analyze a single region on the negative, the negative is positioned in the holder so that the reference point on the negative corresponds to a corner of the segmenting grid. The camera is focused on the negative such that one grid square fills the entire 512 X 512 pixel matrix. The image is digitized and displayed in black and white (128 grey levels) on a monitor. A library program is called up which allows the user to interactively threshold the display to obtain a black and white binary image (2 grey levels) which is required for processing. The operator may try several threshold values defined by the grey level of pixel at the current position of the cursor. The binary image is placed into another buffer so that it can be compared with the real image. A flicker command allows the user to alternately flash these two images on the monitor and verify that the binary image is an adequate representation of the original image. The most representative binary image is subjectively determined by the operator and used for further analysis. If in the analyst's opinion a region of the digitized image does not compare favorably with the original, a more accurate representation can be obtained by repeating the process using an alternate threshold value or by breaking the area into a series of subareas and treating each one separately.

A calibration scheme is necessary in order to determine the full scale size and location of droplets measured on digitized images. The calibration is accomplished by measuring the known distance between the grid lines on the scaling grid and the distance between these lines determined by viewing a photograph of the scaling grid on the image processing system. This allows distance in pixels to be converted to full scale distances in the wave tank.

The size and position of the window where drop diameter is measured may be determined with the segmenting grid. Windows formed by the boundary of an individual segment have been used in our analysis although the system can easily be made to use smaller or larger windows by altering either the size of the cells in the segmenting grid or by sorting data according to actual position. Actual position can be obtained with this system because the software determines the position of the center of each drop inside its particular segmenting grid cell. This allows the position of each drop to be determined relative to the reference mark or any general frame of reference, after which the drops may be sorted in order to isolate those in any particular region of the space that was measured.

IMAGE PROCESSING

A program written in Pascal was developed to determine the location and diameter of drops on a binary image. The program scans any rectangular region identified by the system operator that is part of the digitized image. It begins at the top left corner of the region and scans to the right boundary and then moves to the next row. Once an edge of a drop has been found, a search routine locates the rest of the pixels associated with that drop by examining each pixel on the edge of the first pixel found. A pixel identified to be part of the drop is stored in a "seed" array. Once the four pixels surrounding the first pixel found have been examined, the routine advances to the next pixel or "seed" which is part of the drop and examines the four pixels closest to it. Once a pixel has acted as a "seed" for the identification of its neighbors, it is marked by changing its light intensity value so that it will not be counted again. The program proceeds in this fashion until there are no more "seeds" signifying that all the pixels associated with the drop currently under study have been found. The total number of "seeds" associated with a search is stored and utilized to determine the drop diameter.

Having processed one drop the program resumes the scanning at the point where it first encountered the last drop. As the scanning continues, drops which have been counted are not recounted because they have been marked. The entire region identified for measurement is scanned and all drops measured.

Since the total number of pixels associated with a drop is known, the total area of the drop can be determined using the area of a single pixel. Knowing the total area of the drop and assuming the drop to be a perfect circle, the diameter can be found. The drop's center is used to locate the drop. The row and column coordinates of the center are determined as the mean row or column values of the pixels associated with the drop. This center is a location relative to a corner of the grid segment under study. The drop location relative to the vertical depth in the tank is easily determined from this information by accounting for the displacement of the segment under study relative to the reference mark.

Drops can occur on an edge of a region being analyzed. A routine in this program examines drops which occur on an edge to decide whether they should be counted. If more than half of a drop's area is within the boundaries of the image being studied, the drop is counted. The routine compares the length of a side of the drop occurring on the boundary with the perpendicular distance from the boundary to the pixel farthest from the boundary. Assuming the drop is perfectly circular, the ratio of these values can be used to determine whether the drop is counted. The program is limited only by its capability to properly interpret drops which occur in the corner of

an image and by drops which are connected together. When either of these conditions occurs, the system operator is required to make a decision as to whether the drop should be counted or not. Such drops can be measured manually with a cursor that is interactively manipulated on the monitor screen.

ACCURACY

An analysis was performed to compare the drop diameter measured by the computer with measurements made manually by the operator in order to insure that the above procedure produced reasonable results. An image was digitized and the diameters of the drops on the binary image were determined by the method described above. Diameters of the same drops were also determined manually from the 128 grey level digital image. Manual measurement was accomplished by moving the cursor to individual drops and counting the number of pixels across the region that the analyst judged to be the actual diameter of the drop. Comparison of the pairs of measurements showed that drop diameter determined with the computer program is adequate for the purpose of determining the droplet diameter distributions.

ADVANTAGES/LIMITATIONS

There are a number of distinguishing characteristics that make this an appealing system for use and further development. First, is the ability to measure within a small sample volume without introducing any physical component of the sampling system directly into the flow field where it may disturb the measurement environment. Second, is the relatively uniform illumination of droplets and the lack of illumination of dust and debris that is achieved by making use of the fluorescent characteristics of the oil. Third, is the ability to use a semiautomated approach for the determination of drop characteristics which allows an observer to see that no unusual photographic situation produced erroneous results that contaminate the data. Fourth, is the ability to handle a wide range of drop sizes down to drops as small as 0.2mm.

Of course the system has its limitations, many of which could be overcome with additional development. The principal limitations are the low intensity of the light reaching the film from the oil droplets and the fact that the system is not fully automated so that analysis remains a time consuming process. The low light levels in combination with the short exposure times necessary to stop drop motion limit the magnification that can be achieved between the real drop and the image on the photographic film and thereby limit the size of the smallest drop that can be reliably measured. Additional limitations result from the narrow width of the field where there is sufficient light intensity for photography, the blockage of light to regions farther down field by drops closest to the light source and the inability to record those large droplets which are formed by a thin layer of oil surrounding a large mass of water.

SUMMARY

The physical processes responsible for the dispersion of surface oil are very complex and much research remains to be done before the problem is truly understood. In situ measurement systems that allow the characterization of individual droplets will ultimately contribute to this understanding. One such system has been described. It is not without its limitations

but hopefully further development of such systems will result in better quantification of the processes responsible for droplet dispersion.

ACKNOWLEDGMENTS

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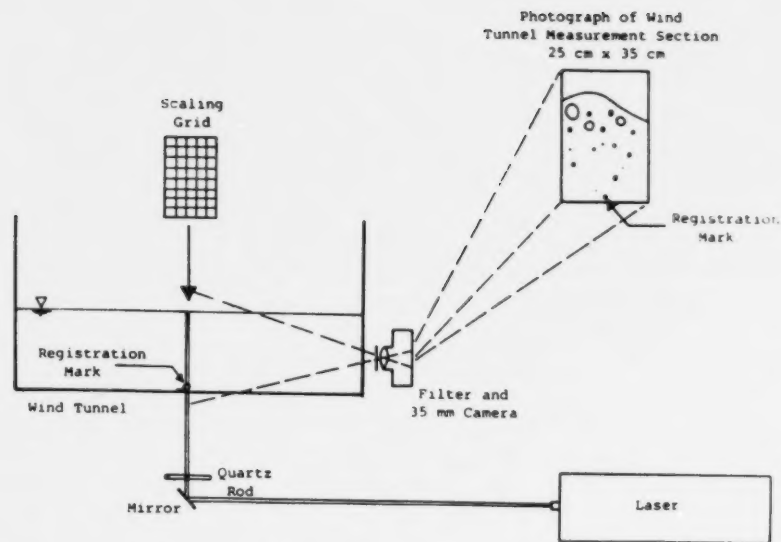


Fig. 1 Schematic Diagram Showing the Photographic System

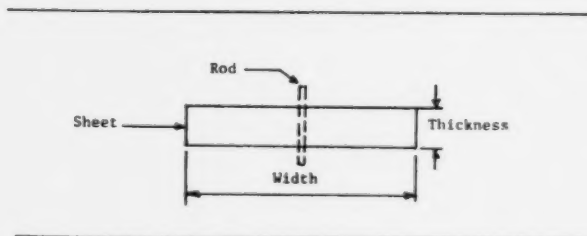


Fig. 2 Laser sheet geometry

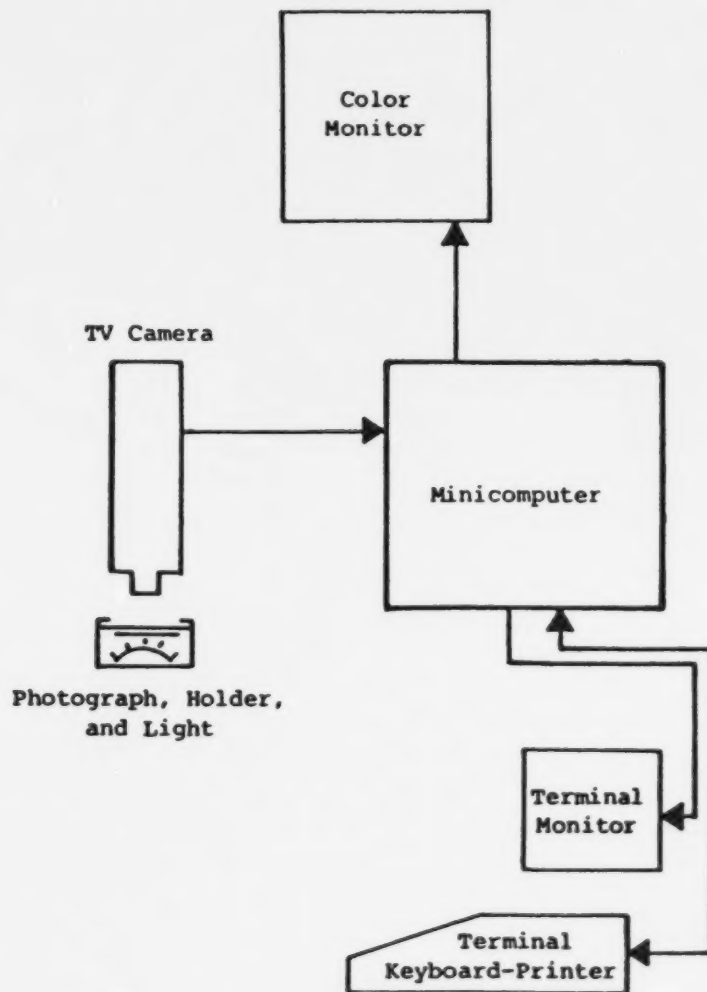


Fig. 3 Schematic Diagram Showing the Image Processing System

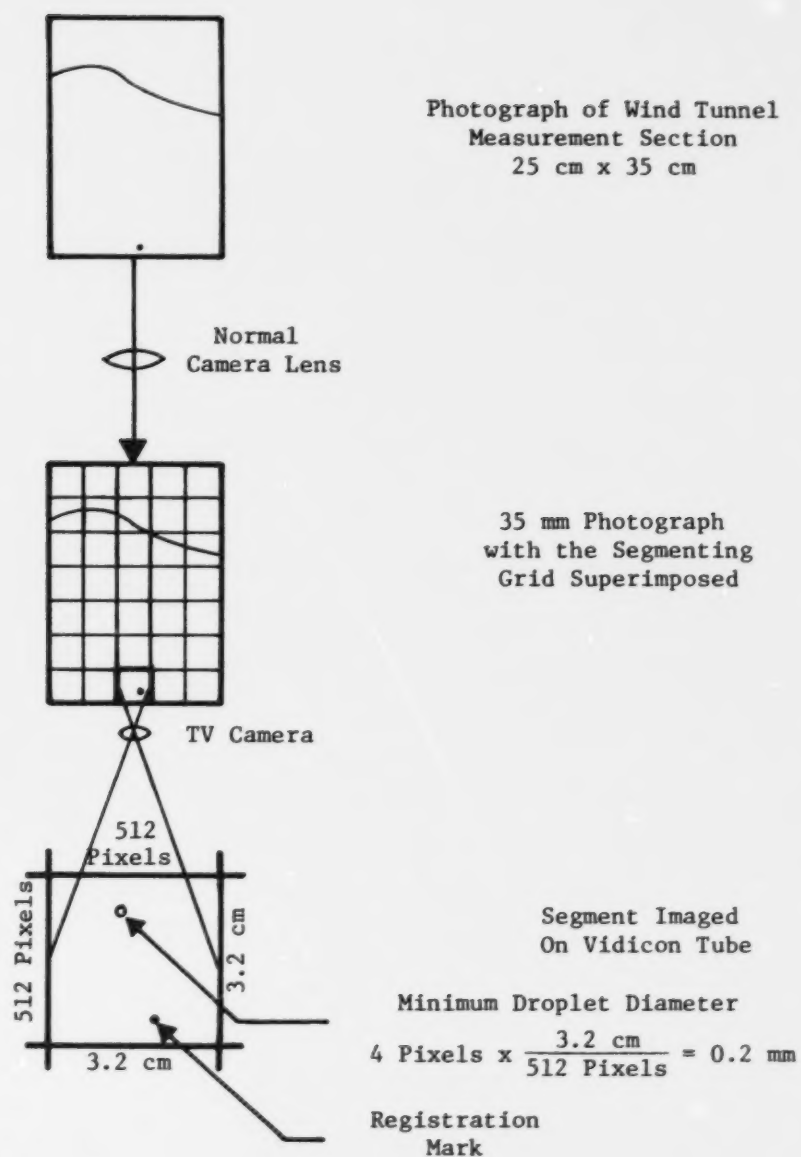


Fig. 4 Schematic Diagram Showing How Camera Lens, TV Lens, and Video Tube Influence Resolution

SATELLITE BUOY TRAJECTORIES, 1982, 1985

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INTRODUCTION

The exploration for oil and gas under the Beaufort Sea has given rise to the possibility that a serious oil spill incident could occur. Even considering the recent drop in world oil prices, one can expect that exploration will continue to some extent. If a spill does occur, the ability to predict the movement of the spilled oil on water or with ice will be of utmost importance.

Since 1979, the Coast Guard Research and Development Center (RD&C) has had an ongoing research program to determine the surface currents of the Beaufort Sea (Figure 1). The results of satellite buoy work in other years were presented by Murphy, et al. (1981), Murphy, et al. (1983), and Robe, et al. (1984).

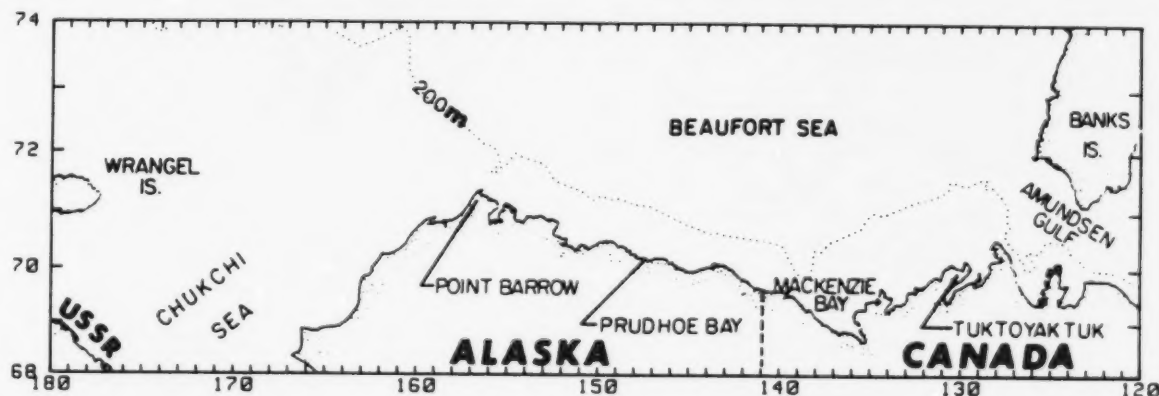


FIGURE 1. STUDY AREA

The Coast Guard's work in this program has been in cooperation with Canadian Marine Drilling, Ltd. (CANMAR), a subsidiary of Dome Petroleum.

BACKGROUND

The earlier work with satellite-tracked buoys, which covered buoy years 1979, 1981, 1983, has confirmed that the generalized drift of ice and the sea surface is in an east/west direction. Although the majority of the movement is from east to west, periods of west to east movement were observed. Buoys were either released north of Prudhoe Bay, or northwest of the Tuktoyaktuk Peninsula.

BUOYS

The drifting buoys used during the 1982 experiment were the CANMAR type described in Murphy, et al. (1983). They consist of a 1.12 m diameter hull with an 0.2 m. drag skirt. This allows these buoys to float nearly awash. The buoys released during the 1985 drift experiment were spar buoys which consisted of a 3 meter long metal hull with a bulbous upper section for buoyancy topped by a fiberglass antenna. Buoys were not drogued in either year.

Tracking was done by the TIROS/ARGOS system using the TIROS series satellites. Positions were determined from data processing by Service ARGOS. Positions are better than ± 150 m at one standard deviation and ± 500 m at three standard deviations. At least nine positions per day can be expected at Beaufort Sea latitudes (Robe, et al., 1984).

DATA PROCESSING

Data were processed by separately converting the records of latitude and longitude into equally time-spaced (3 hours) records using a four-point linear interpolation scheme. These were then filtered, when possible, using a low-pass filter with a cut-off of 116×10^{-5} Hz (one cycle per day). This filtering removes the random errors and a majority of the tidal and inertial effects (Robe and Maier, 1979). Speed and direction of buoy movement were computed at 3-hour intervals.

1982 BUOY RELEASES

In September 1982 four CANMAR type buoys were released northwest of the Tuktoyaktuk Peninsula. Buoy ID's were 4505 through 4508. Figures 2 through 5 depict the filtered data track of each buoy respectively. Figures 3-5 show the Beaufort Sea area from 69°N - 72.5°N latitude and from 128.5°W - 155.5°W longitude. Buoys 4506 through 4508 follow similar westward paths for the first 3 weeks of drift. At that point all three buoys moved in a more southeasterly direction for 10-14 days. About that time, the path of buoy 4507 continued eastward and ran aground along the Canadian coast. Buoys 4506 and 4508 reversed direction and travelled westward approximately 25 km off the Alaskan Coast. The signal of buoy 4508 was lost on 19 October, but buoy 4506 was tracked along the coast to a point north of Smith Bay, Alaska, until lost on 26 January 1983.

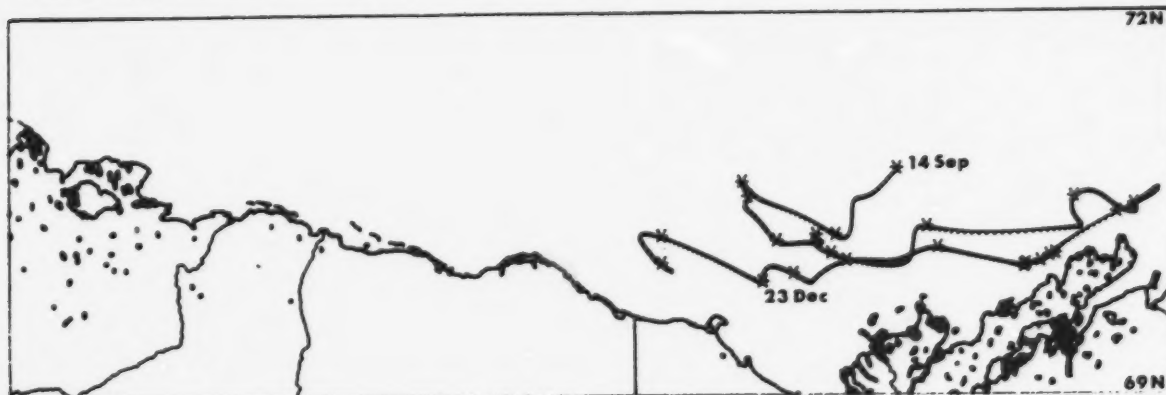


FIGURE 2. TRACK OF BUOY 4505



FIGURE 3. TRACK OF BUOY 4506.

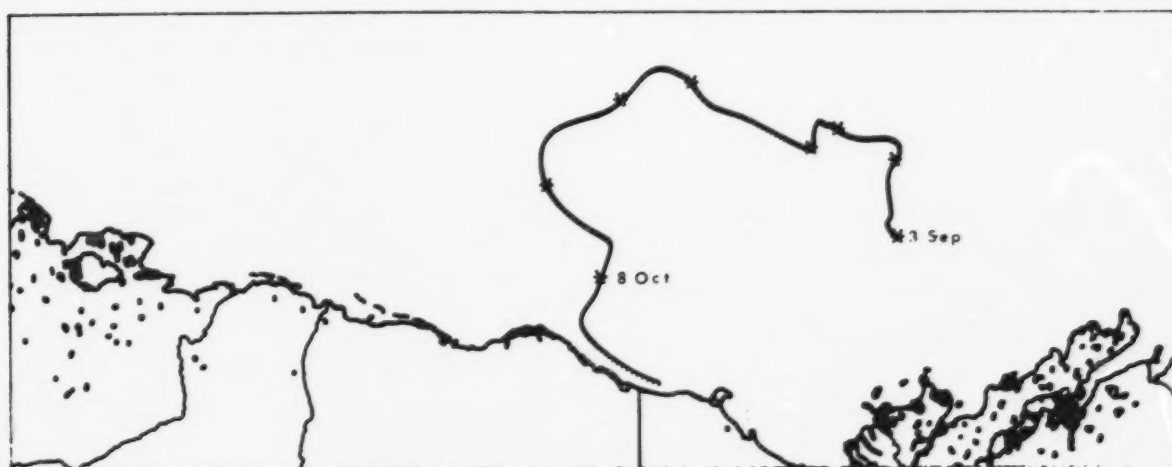


FIGURE 4. TRACK OF BUOY 4507.

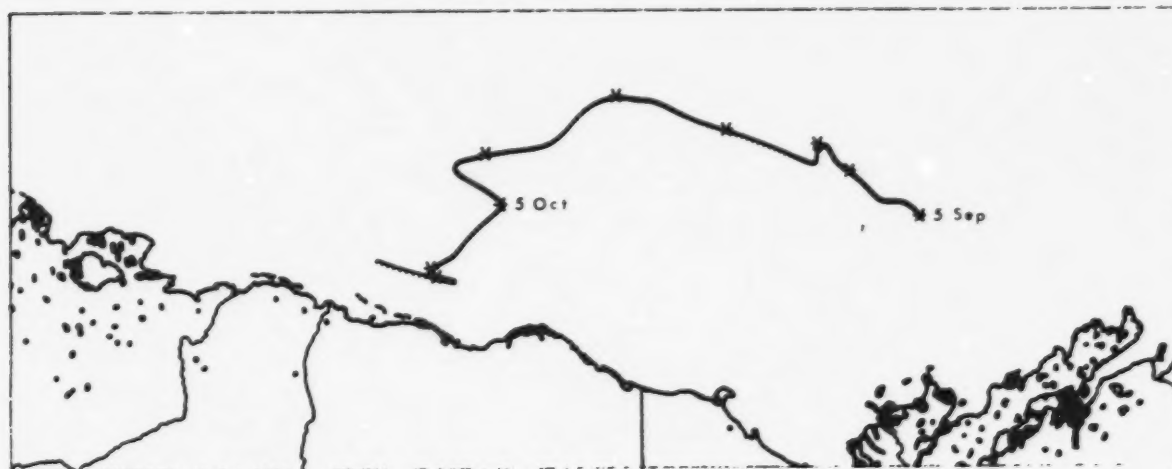


FIGURE 5. TRACK OF BUOY 4508.

Buoy 4505 had a much different track than the other three drifters. It first moved southwest for 5 days, then changed to a northwestward movement for 5 days. It then reversed direction for approximately 5 weeks until it reached a point north of the tip of the Tuktoyaktuk Peninsula. Direction was reversed again and it travelled in a westerly direction for 7 weeks until it moved in a southeasterly direction for 1 week when the signal was lost on 10 January 1983.

Speed and Direction

Histograms of speed and direction for all four buoys are presented as Figures 6 and 7. Speed histograms are shown first for buoys 4505 through 4508, respectively (Figures 6a-6d), followed for the applicable direction histograms (Figures 7a-7d).

For buoys 4505 and 4506, the greatest frequency of speed fell in the 0-8.5 cm/sec range, dropping off in frequency with increasing speed. In contrast buoys 4507 and 4508 have the greatest frequency in speed in the 8.5 to 25.5 cm/sec range. The differences in these frequencies, especially comparing buoy 4506 to 4507 and 4508, are primarily due to the greater length of recorded drift for buoys 4505 and 4506. During these buoys' drift history, there were often periods of little to no movement followed by periods of very rapid drift.

The direction histograms for these buoys do not provide a great deal of insight. As expected, the greatest frequency of direction fell in the east or west direction for all four buoys. Buoy 4508 is somewhat different in that none of the recorded movement was in the 000° to 090° sector.

Figures 8a through 8d are plots of speed versus direction for buoys 4505 through 4508, respectively. For buoys 4505 through 4507, the greatest speeds are recorded in either an east or west direction. Buoy 4508 is different in that there was less easterly movement and when it occurred it was at a slower speed (10-25 cm/sec versus 50-70 cm/sec) than the other buoys. This could again be partially due to the shorter drift time of buoy 4508 as compared to 4505 or 4506.

Comparison of Geostrophic Wind

Geostrophic winds were calculated from 12-hour synoptic surface isobar charts of the Beaufort Sea. Only the U component of the wind was calculated and adjusted for the directional effects of the earth when determining sea level values. The wind was not adjusted for rotation as it was felt that this correction was much less than the error inherent in computing wind from synoptic charts. The reciprocal of this value was compared to the component of buoy movement (u) for 12-hour filtered positions. Figures 9a through 9d depict these comparisons. The wind component has been multiplied by a factor of 10 to allow for a better visual inspection of the data. A statistical analysis of the data showed that there were no significant correlations between U and u for any of the buoys. Table 1 shows these values.

TABLE 1. CORRELATION COEFFICIENTS FOR U VS. u

Buoy	r
4505	.2416
4506	.2998
4507	-.1803
4508	-.1814

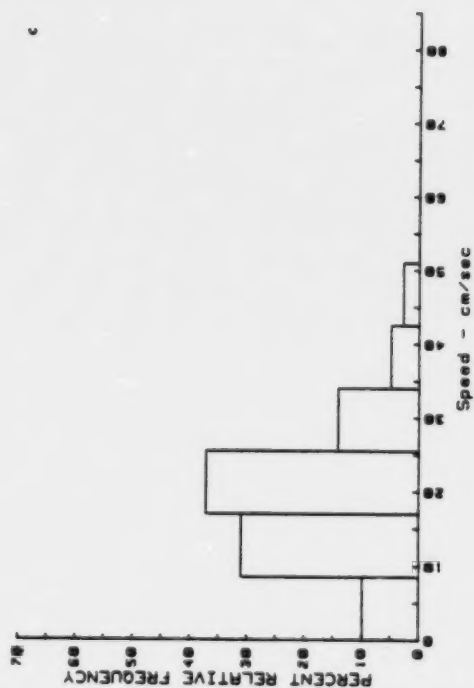
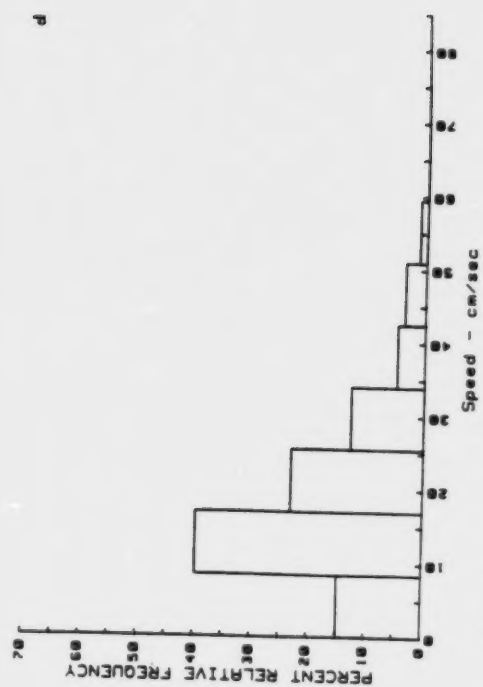
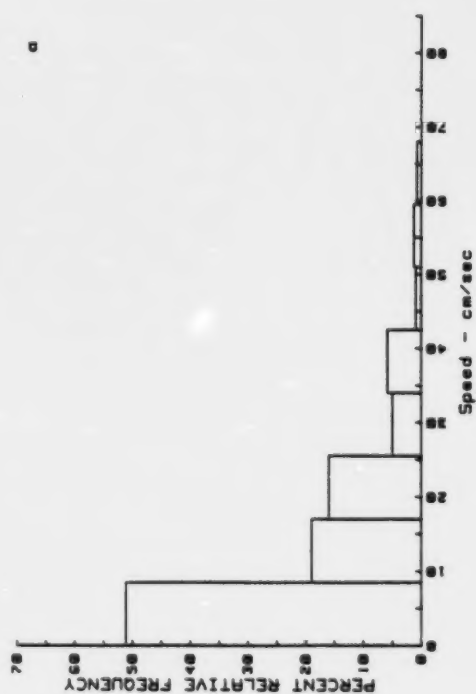
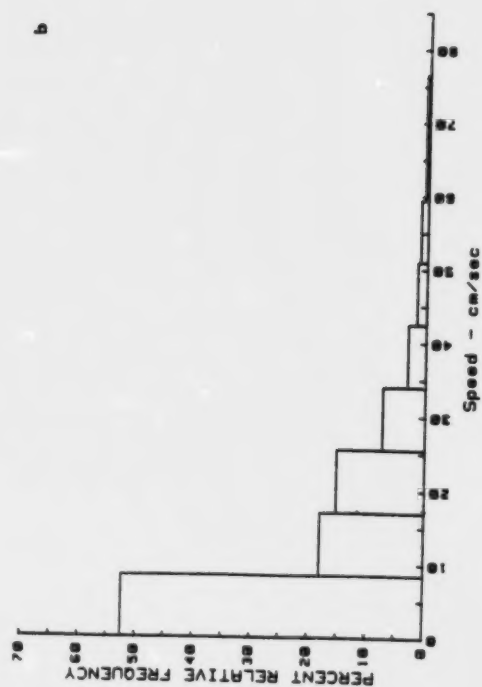


FIGURE 6. HISTOGRAMS OF SPEED FOR BUOYS 4505 (a), 4506 (b), 4507 (c), AND 4508 (d).

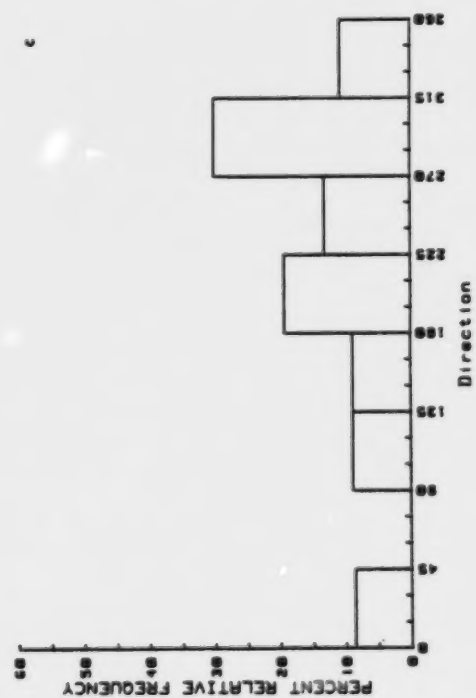
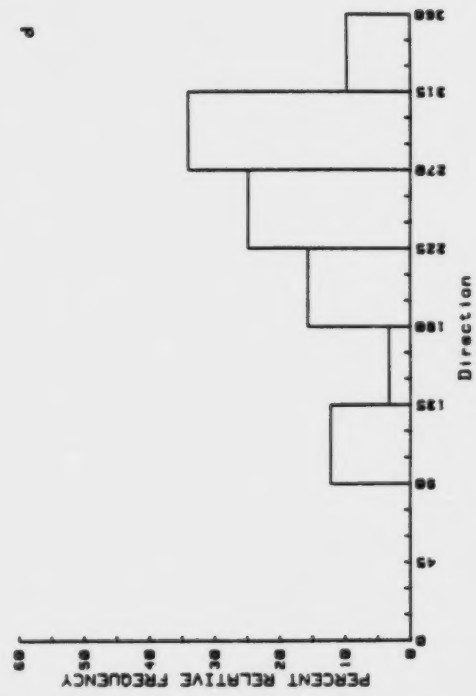
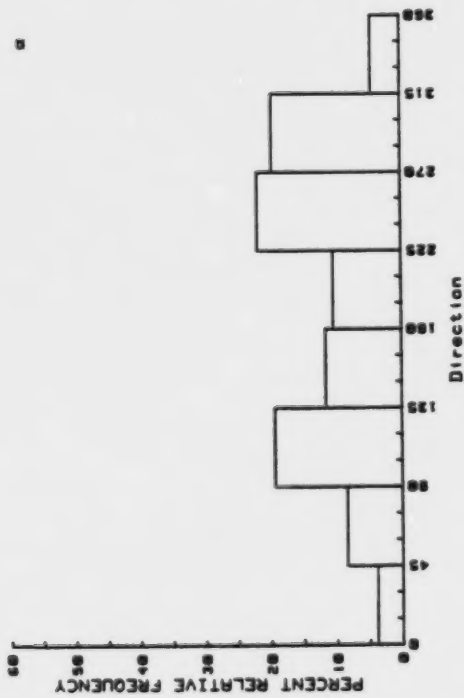
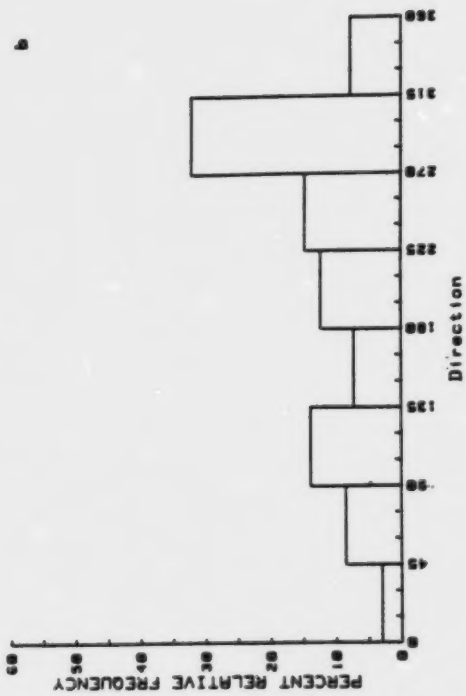


FIGURE 7. HISTOGRAMS OF DIRECTION FOR BUOYS 4505 (a), 4506 (b), 4507 (c), AND 4508 (d).

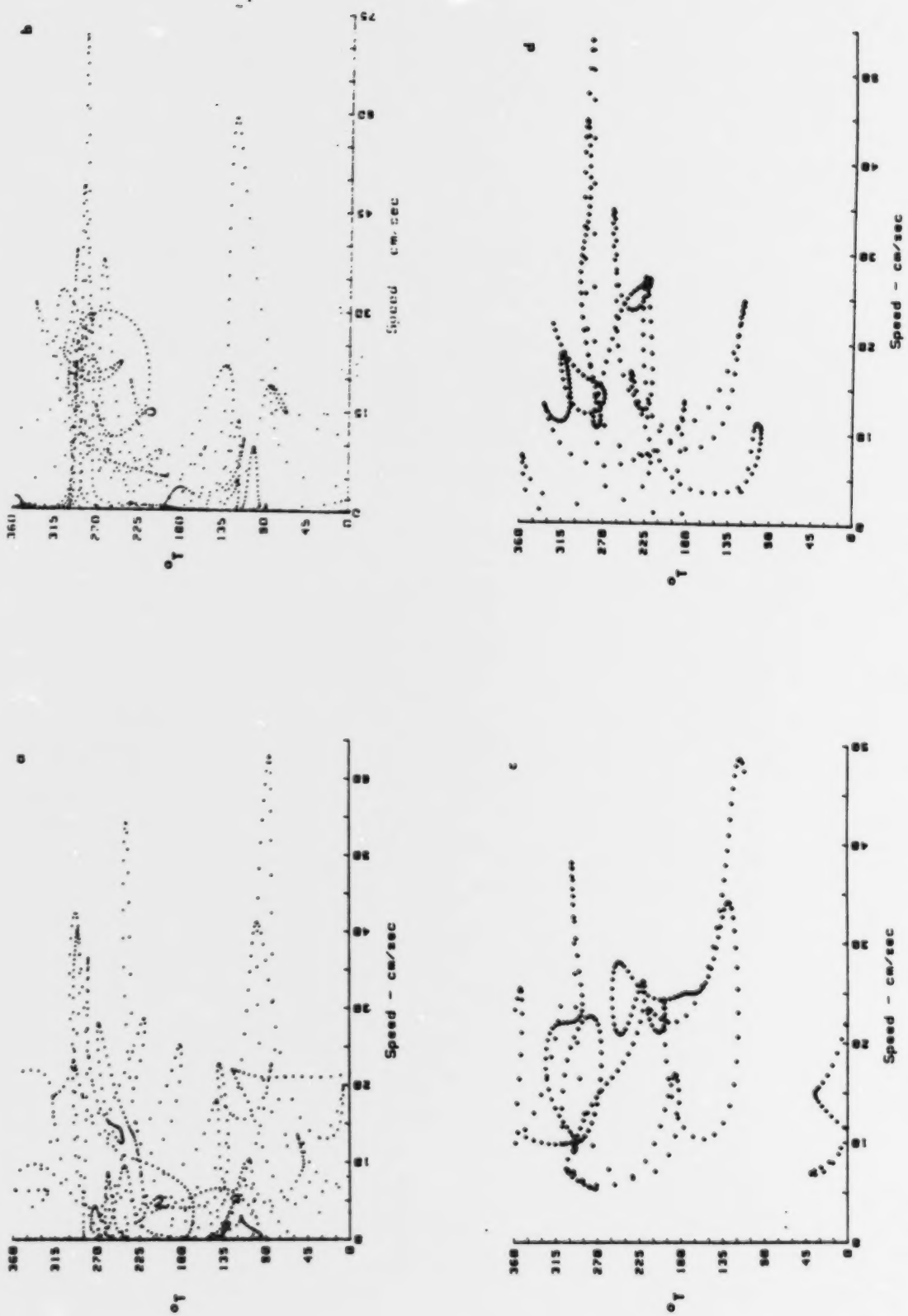


FIGURE 8. SPEED VERSUS DIRECTION FOR BUOYS 4505 (a), 4506 (b), 4507 (c), AND 4508 (d).

An examination of Figures 9a through 9d reveals that there were some noticeable events where the buoy movement would follow a wind event with a lag of approximately 2 days. These events occurred on 18 September, 22 September, and 3 October, which are designated on Figure 9d (buoy 4508).

Separation Versus Time

An analysis of the horizontal separation of buoys 4506, 4507 and 4508 over time was also conducted. Separations were calculated at 3-hour intervals for those times where data overlapped. Buoy 4505 was not included in this analysis because of its radically different drift pattern.

Buoys 4506 and 4507 began at a distance of 85 km apart (Figure 10a). The separation initially lessened to a minimum of 35 km and remained fairly steady for 8-10 days. The separation then jumped to about 60 km and remained at that level for another 8-10 days. The separation then rapidly increased to over 250 km at the end of usable data. This rapid separation was due to buoy 4507 drifting eastward along the coast while buoy 4506 drifted westward.

Buoys 4507 and 4508 began at a separation of approximately 22 km (Figure 10b). This separation remained in the 20-45 km range for the first 18 days of data. At this point, the separation between these buoys steadily increased (approximately 2 km/day) until day 30 where the separation rapidly increased. This rapid increase in separation was again due to the eastward trend of movement in buoy 4507 as compared to buoy 4508's westward movement.

The comparison between buoys 4506 and 4508 (Figure 10c) provides an interesting comparison of buoy movement. Both buoys exhibited similar overall drift tracks. Buoy 4506 did drift in a much more looping pattern than buoy 4508, however. This looping can explain the wide variations with time of the separation between these buoys. Otherwise, there is no apparent pattern to the "sine-like" pattern in these buoys separation over time.

The relative movements of these buoys over time are affected by many dynamic forces. Variations in the local wind field, surface layer fronts, eddies, and ice flow patterns, when present, all interact in driving the movement of each buoy. Without adequate measurement of these variables, it is difficult to determine which forces were involved in the differences in movement of each buoy. The benefit of these comparisons, however, is in determining whether there is any evidence of similar forces on these buoys over time. In general, the forces on each buoy appear to be generally independent, except for short periods when certain buoys seemed to have moved in similar directions and speeds (i.e., buoys 4506 and 4507).

An analysis of the correlation coefficient (r) between the distance between buoys and time elapsed for each of these comparisons yielded the results of Table 2.

TABLE 2. CORRELATION COEFFICIENTS (r) FOR DISTANCE VS. TIME

Buoy	r
4506-4507	.7343
4507-4508	.8363
4506-4508	-.4907

As expected from reviewing Figures 10a-10c, the analysis of buoys 4506-4507, and 4507-4508 yielded a strong correlation for distance generally increasing with time. These values may be skewed higher than would otherwise be expected if not for the end of each data record where distance is increasing steadily with time. However, for these comparisons, the analysis

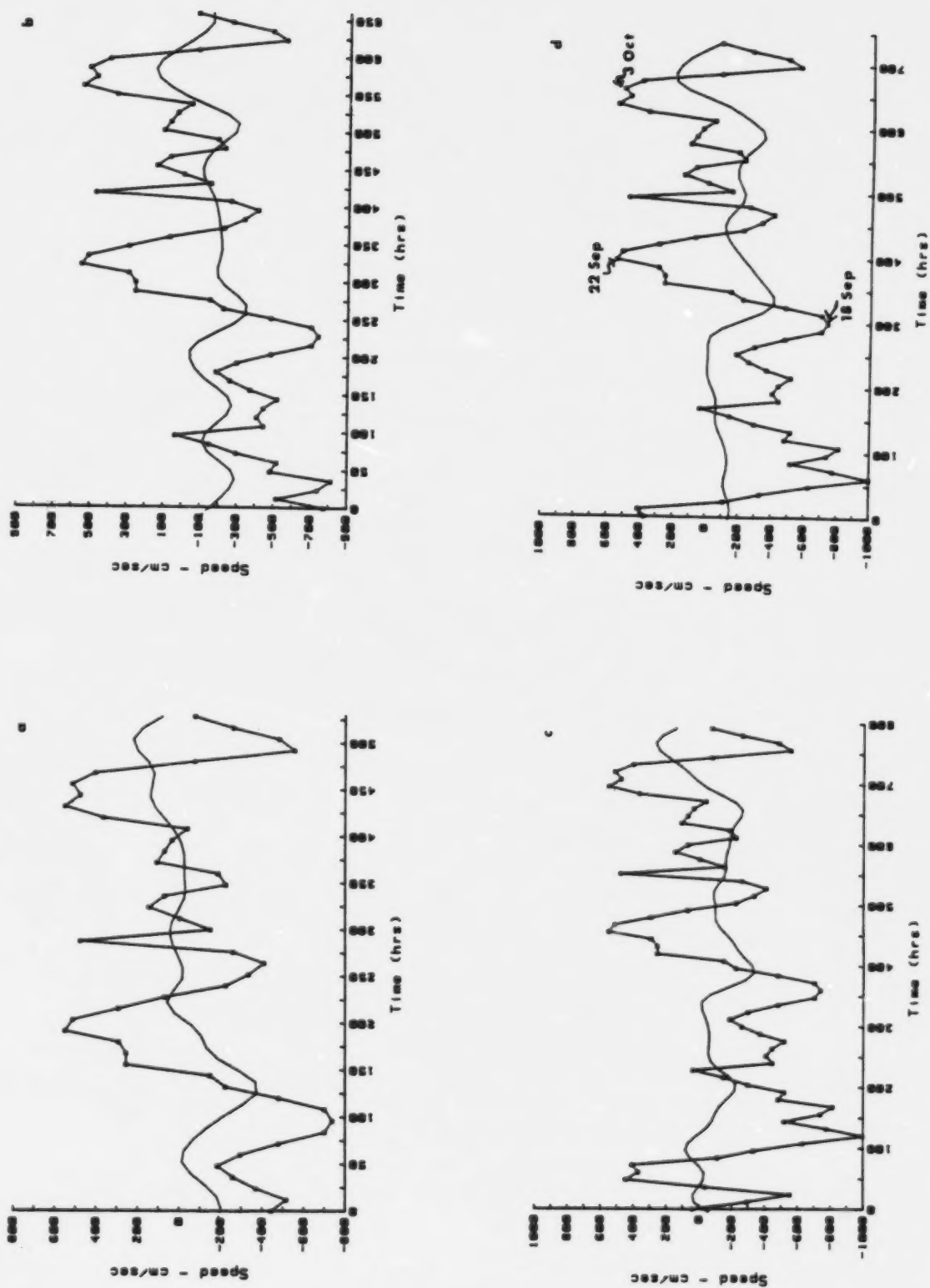


FIGURE 9. COMPARISONS OF U-DIRECTION WIND SPEED TO U-DIRECTION BUOY SPEED FOR BUOYS 4505 (a), 4506 (b), 4507 (c), and 4508 (d). BUOY SPEED (SOLID LINE) HAS BEEN INCREASED BY A FACTOR OF 10.

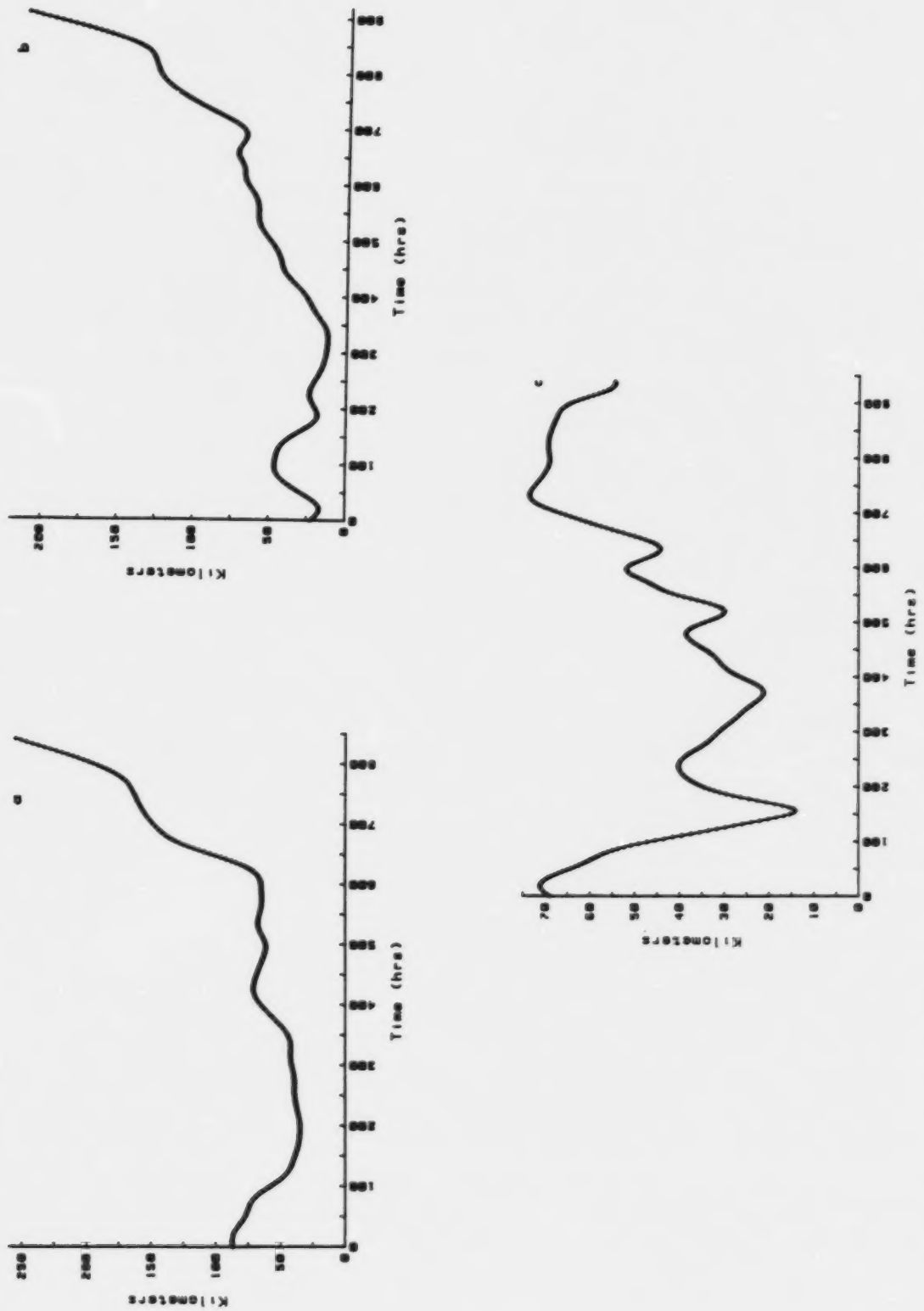


FIGURE 10. SEPARATION BETWEEN BUOYS OVER TIME FOR BUOY PAIRS 4506-4507 (a), 4507-4508 (b), AND 4506-4508 (c).

has revealed that the forces on buoy 4507 (which eventually moves rapidly west) are different from those on either 4506 or 4508. Buoys 4506 and 4508, though, have forces which resulted in a more similar movement and the consequent lower correlation value. Overall, these two buoys moved in a similar pattern over time.

1985 Buoy Releases

Three buoys, ID numbers 4538, 4539, and 2581, were released on 9 August 1985 to the northwest of Prudhoe Bay. All three buoys were undrogued. The buoys were deployed from the oil spill recovery vessel ARCAT in 6-8 oktas of ice approximately 10 km and 2 hours apart. During the deployments, surface currents were observed to be flowing at several cm/sec to the south. A sample of this water was tested at 15‰ salinity. It is believed that some of this surface layer movement was due to the melting of the edge of the polar ice cap (which was within 40 kilometers of Prudhoe Bay). All three buoys were also observed moving with this surface layer and rapidly overtaking the large pieces of ice in the area.

During the first few days of drift, all three buoys moved westward then reversed direction and ran aground along the Beaufort Sea coast (Figures 11a-11c). Buoy 4538, the first to be released, was apparently caught among ice for a few days before it was able to begin its initial westward drift. Buoys 2581 and 4539 ran aground along the Return Islands while buoy 4538 ran aground within Prudhoe Bay. Buoy 2581 was sighted by an oil service company tugboat and recovered. This allowed for the redeployment of 2581 on 25 August. The subsequent movement of this buoy will be presented later. The first few days of this buoy's drift will henceforth be designated as buoy 2581a.

Buoys 2581a and 4539

Buoys 2581a and 4539 exhibited similar movement during the short time until they ran aground. Interestingly, buoy 2581a, which was deployed last and at the westward-most point, spent approximately 15 hours in the vicinity of Beechy Point. During this time of little movement, buoy 4539 was steadily moving west towards the location of buoy 2581a. Both buoys then were transported towards the southeast, with buoy 2581a moving farther east before running aground. The result of this relative movement between buoys 2581a and 4539 can be seen in Figure 12. These buoys began their drifts 9.5 kilometers apart. After 33 hours, they were only 1.5 kilometers apart, after which the distance between them increased to 10 kilometers when they both grounded. One possible explanation for this movement is that a front formed in this vicinity in the upper surface of the Beaufort Sea. This could explain the continued movement of buoy 4539 while 2581a remained relatively motionless. When both buoys had reached the frontal area (at their closest relative distance), the wind/current dynamics may have changed to move these buoys to the southeast and aground.

Surface wind data was being recorded at this time at the Deadhorse Airport and at Resolution Island. The mean wind speed and direction recorded at these locations for 10-12 August 1985 are listed in Table 3. As shown, wind shifted from easterly to westerly and back again during this period. Since one can expect a lag in the change in current direction after a wind shift, these shifts can explain the movement of the buoys southeastward (due to the westerly wind on 11 August). The subsequent shift of the wind on 12 August could explain the buoys moving aground as the current was beginning a change in direction.

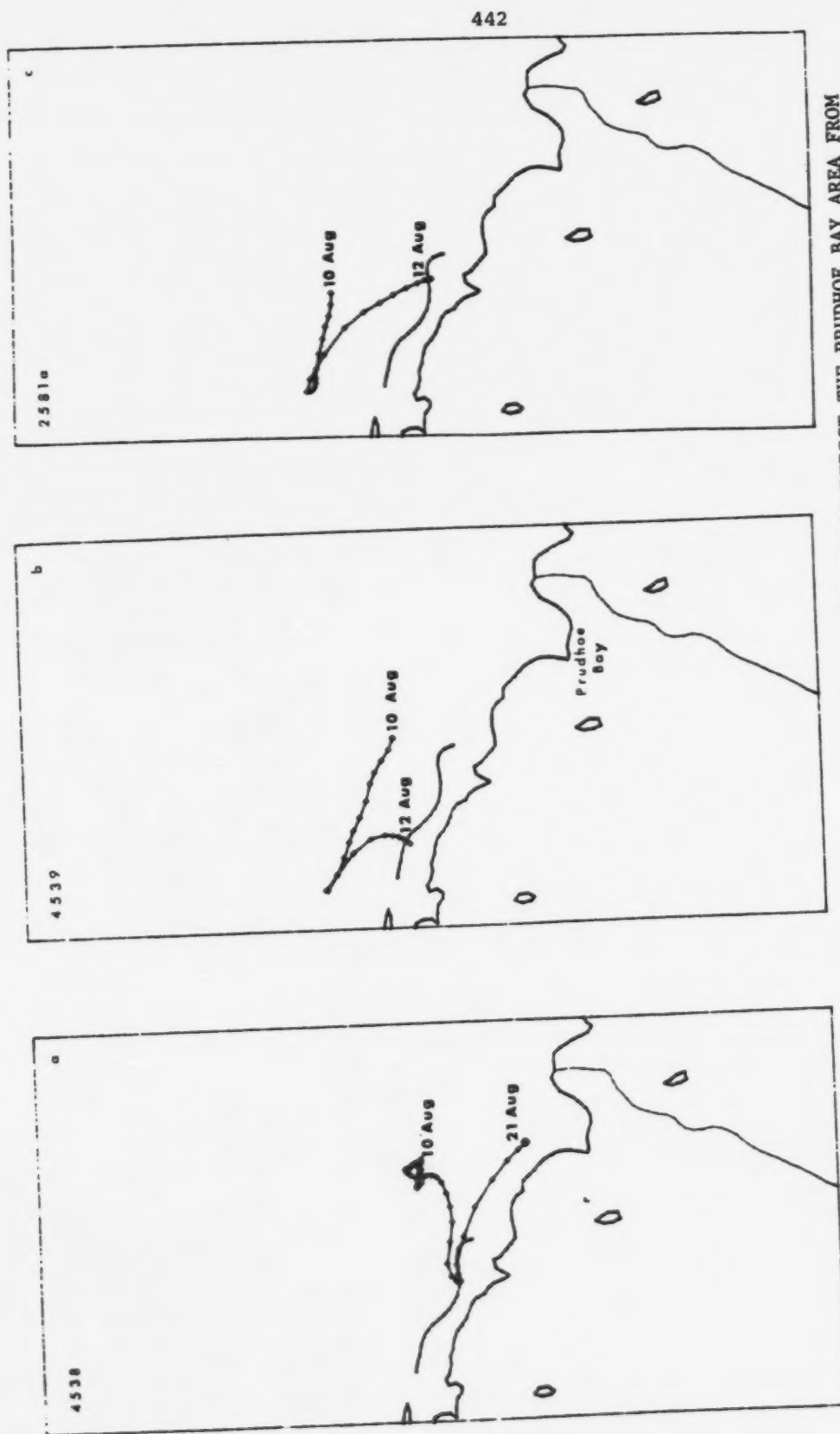


FIGURE 11. TRACKS OF BUOYS 4538 (a), 4539 (b), AND 2581a (c). ALL THREE DEPICT THE PRUDHOE BAY AREA FROM 70°N - 71°N LATITUDE AND FROM 148°W - 149.5°W LONGITUDE.

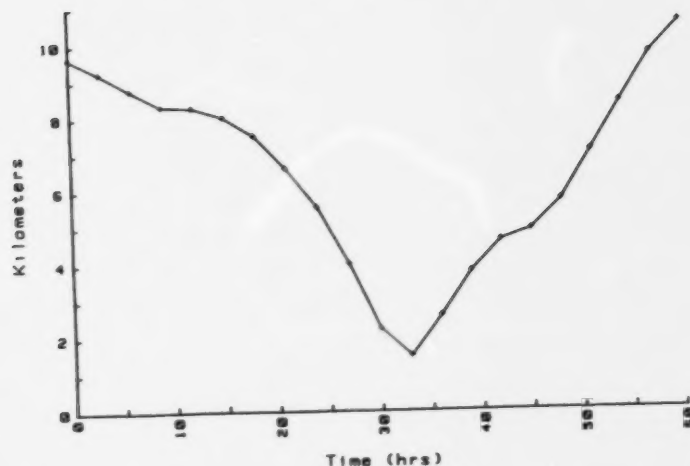


FIGURE 12. SEPARATION VS. TIME OF BUOYS 2581a and 4539

TABLE 3
AVERAGE WIND SPEED AND DIRECTION AT DEADHORSE AIRPORT
AND RESOLUTION ISLAND FOR 10-12 AUGUST 1985
(HACHMEISTER, 1986)

		10 August	11 August	12 August
Resolution Island	Speed (m/s)	5.49	4.21	4.08
	Direction ($^{\circ}$ T)	073.5	293.2	060.9
Deadhorse Airport	Speed (m/s)	5.3	5.69	4.7
	Direction ($^{\circ}$ T)	068.5	281.2	065.0

Buoy 4538

Buoy 4538, as depicted in Figure 11c, did not move very far from its deployment location for several days. Once it did begin to move southwestward (on 16 August) it followed a path towards the Return Islands and then reversed direction on 18 August to run aground within Prudhoe Bay. Wind data from Hachmeister (1986) indicates that the wind did shift clockwise from a northerly to westerly direction during this period. This wind shift can explain the movement of this buoy.

Buoy 2581b and 2581c

On 25 August 1985, buoy 2581 was redeployed to the northwest of Prudhoe Bay. It traveled west until it ran aground in the vicinity of Harrison Bay on 5 September. This segment of buoy 2581's drift has been classified as 2581b. It is shown as Figure 13.

On 17 September this buoy broke free and began to move west. It has continued to drift and send position signals ever since. Figure 14 shows this segment of drift which has been designated 2581c and is shown until cut off on 31 March 1986.

Since no wind information is presently available for an analysis of these drift segments, they have been presented for informational purposes only.

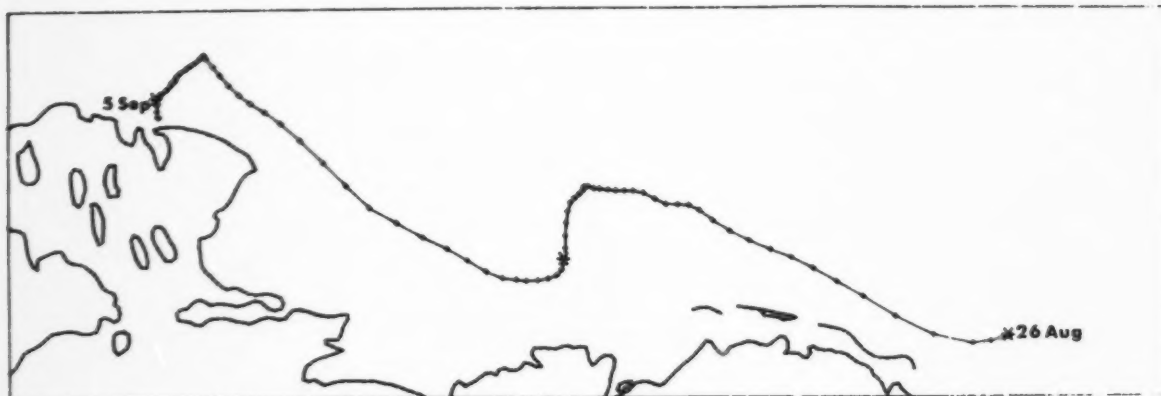


FIGURE 13. TRACK OF BUOY 2581b

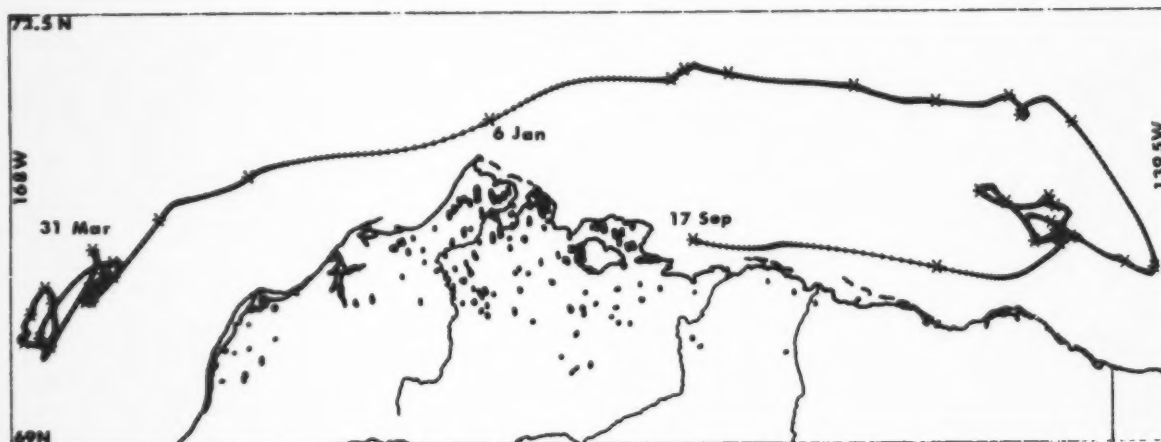


FIGURE 14. TRACK OF BUOY 2581c

CONCLUSION

As was seen in the movement of buoys which were deployed in 1979, 1980, 1981, and 1983, the movement of the buoys examined here was generally along the Beaufort Sea coast. A further analysis of movement in comparison to available wind and local ice conditions should reveal a better dynamic picture of the factors involved in the drift of these buoys. A comparison of buoy trajectories to both the U and V wind fields may reveal a high correlation, with an expected lag, of these variables. Spectral analysis of these data may also reveal some of the factors involved in the dynamics of the surface layers in the Beaufort Sea. These types of analyses have not been conducted for all six years of buoy data, but will be in the future.

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EVALUATION OF REMOTE SENSING SENTINEL INSTRUMENTATION FOR DETECTING OIL DISCHARGES FROM OFFSHORE PLATFORMS

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ABSTRACT

A permanently mounted, remote sensing instrument is an attractive means of monitoring offshore oil and gas platforms for oil discharges. This paper discusses the evaluation of three possible sentinel systems: an active infrared sensor, an infrared camera and an oil vapour detector.

The evaluation began with indoor testing at a tower tank facility where the sensors were mounted 10 m above the water surface. Sensor responses using a variety of oil types and under a number of different oil and water temperature regimes were determined. Field testing was then conducted along the shore of Halifax Harbour where the sensors were mounted on a moveable platform and up to a height of 20 m overtop the water. During a period of three weeks, the sensors were tested under a range of atmospheric, oceanographic and oil film conditions.

The results showed that the active infrared sensor was capable of detecting oil slicks under most conditions and generating an alarm signal. The IR imager could 'see' oil under most conditions, but interpretation of the picture was required and the instrument was not useful as an alarm. The vapour detector was ineffective.

INTRODUCTION

With the possibility of oil and gas production occurring in three major offshore locations within Canada, the design of a sentinel monitoring system for sensing oil discharges remotely is under consideration.

Such a system would monitor the water surface in the vicinity of the offshore platform for oil films, and trigger an alarm when an oil film was detected. The system would be required to have a low false alarm rate and the ability to operate under a wide range of environmental and illumination conditions.

This is the third in a phased series of investigations to develop an effective sentinel oil monitoring system for deployment on offshore platforms. The first study (Bercha, 1984) detailed a wide range of airborne remote sensing systems that had been used in oil slick detection and mapping. The second study (Martec, 1985) undertook a field evaluation of four sensor systems. A pyro-electric vidicon system was tested but had insufficient sensitivity to detect oil at all times. Low Light Level Television filtered for detection in the near ultra-violet produced good daytime results but was ineffective at night when reflected lights caused it to reduce sensitivity. Problems were encountered with both the Barr and Stroud Infrared Imager and the Oilspills sensor and as a result, a full evaluation of these two units was not possible. Photography in both the visible and near ultra-violet were found suitable for daytime documentation purposes.

This paper describes the Phase Three study which included both a literature search and an evaluation of three remote sensing systems. The literature search reviewed instrumentation suitable for use as a sentinel system. These included a wide range of sensors including in situ floating devices and short-range

oil detection devices that had not been considered in Phase One. One device, a type of active infrared sensor, was identified which showed the best promise for application in offshore oil monitoring. The evaluation therefore included this device and the two other devices that had not been fully evaluated in Phase Two. A standard 35 mm photographic camera was used for documentation purposes. Each of these sensors is described below.

Active Infrared Sensor

The active infrared sensor tested was the Wright and Wright Infrared Oil Film Monitor. This instrument illuminates the water-oil surface with a broad band light source and analyses the reflected radiation in two narrow wavebands. It relies on the dramatic shift in the reflectivity of water due to water molecule absorption in the region 2.0 to 4.0 μm (see Figure 1). A simple OIL/NO OIL decision is made based on the ratio of the signals in the two spectral channels.

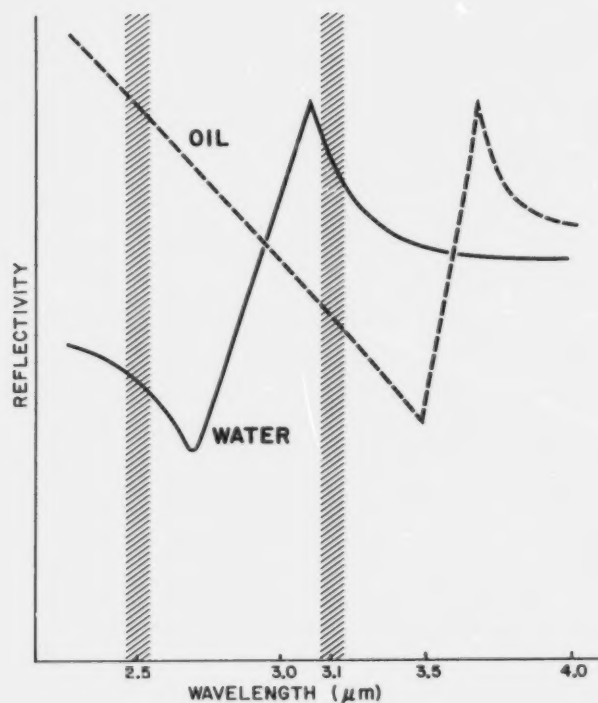


Figure 1. Spectral Reflectance of Water and Oil (wavebands used by the Wright and Wright Infrared Oil Film Monitor are shown as shaded areas) (from Flanagan et al., 1975)

The Wright and Wright Infrared Oil Film Monitor (Figure 2) consists of one or more focused tungsten-halogen lamps, a receiver and a chart recorder. Output from the receiver includes signals from the two spectral channels as well as the ratio channel, all which are available as 0-10 VDC analog signals.

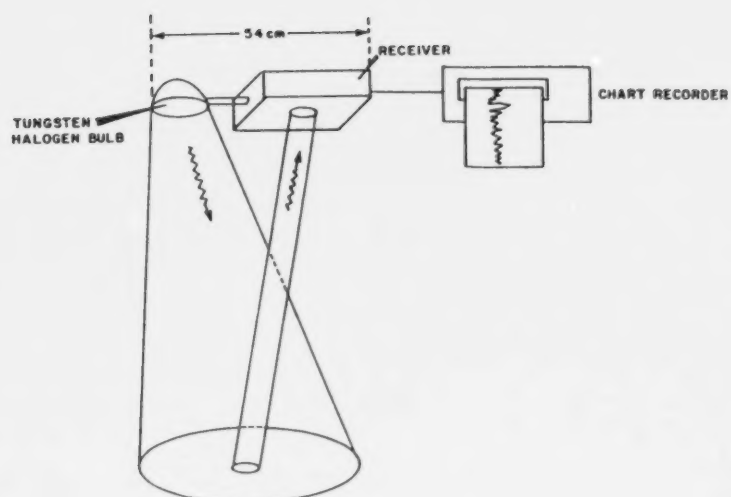


Figure 2. Wright and Wright Infrared Oil Film Monitor (from Martec 1985)

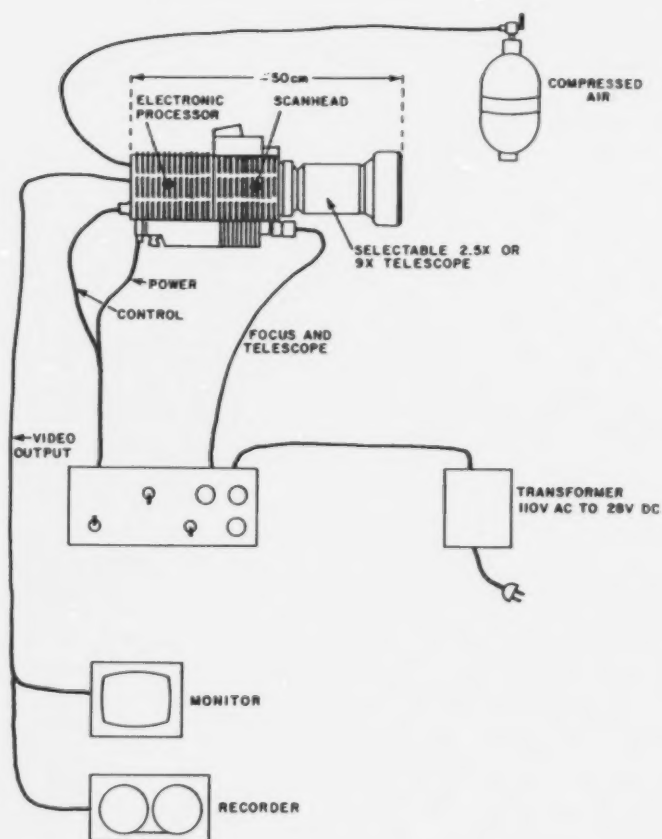


Figure 3. Barr and Stroud Thermal Imager Model IR18 (from Martec 1985)

A selectable alarm relay is included. Specifications for the Infrared Oil Film Monitor are given in Table 1.

TABLE 1
SPECIFICATIONS FOR WRIGHT AND WRIGHT INFRARED OIL FILM MONITOR

Minimum film thickness detected	0.1 micron average thickness.
Area monitored	An area directly below the instrument with a diameter 0.05 times the height of the instrument above the water.
Size	54 cm long x 30 cm wide x 22 cm high.
Weight	8.2 kg with one transmitter,
Outputs	0-10 VDC analog output.
Operating temperature	-18°C to +38°C.
Wavelengths detected	Narrow regions centered at 2.5 and 3.1 microns.
Power requirements	105 - 125 VAC 60 Hz.
Power consumption	
Transmitter	2 x 250 watts + 1 x 500 watt.
Receiver	8 watts.
Options	film thickness discriminator to differentiate thin sheens or thick slicks (greater than 10 microns). Selectable criteria alarm to delay oil alarm until a preset duration is met. Multiple transmitters. Explosion-proof housing.

Past applications of Wright and Wright Infrared Oil Film Monitors have involved deployment in drainage channels from refineries or oil transfer stations. They are usually mounted 2 metres above the water surface. The present test used a newly developed model with a thermoelectrically cooled detector which greatly increased the instrument sensitivity. Performance of this new instrument with greater operating heights, when waves were present on the water surface, and during conditions of reduced atmospheric transmittance were the three most important parameters that required definition.

Thermal Imager

The thermal imager that was evaluated was the Barr and Stroud Thermal Imager Model IR18. The sensor is shown in Figure 3 and specifications are included in Table 2. It consists of a selectable 2.5 or 9x telescope, a scan head and an electronic processor. Ultra-pure compressed air and a Joule-Thompson minicooler are used to cool the detector array. Output is in the form of a signal suitable for display on a standard television monitor.

The Barr and Stroud Thermal Imager detects thermal infrared radiation in the 8-14 μ m waveband. In this region, objects are detected according to their apparent temperature. Apparent temperature is a function of the object's absolute temperature and spectral emittance. Spectral emittance is the efficiency of a target as a thermal radiator.

TABLE 2
SPECIFICATIONS OF BARR AND STROUD THERMAL IMAGER

	<u>Without Telescope</u>	<u>2.5x</u>	<u>9x</u>
Horizontal Field of View	38.2°	15.4°	4.2°
Vertical Field of View	25.5°	10.2°	2.8°
Pupil Diameter	14.5 mm		
Maximum resolution of temperature (at 0.289 cycles/m rad)	0.17°C - 0.5°C		
Detector	Serial/parallel Sprite cooled to 77°K		
Spectral bandwidth	8.0-14 μ m		
Video output	CCIR compatible 1 volt composite video (75 ohm load)		
Display	525 TV lines/frame		
Field rate	60 Hz		
Frame rate	30 Hz		
Cooling requirement	Clean air to AvP32 standard 1/8 in. B9P60° Internal cone inlet		
Inlet pressure	4500 psi max at 25°C 1500 psi min		
Power supply requirements	24 volts d.c. nominal 20 volts min - 32 volts max		
Power consumption	32 watts at 28 volts typical		
Weight			
Scan head unit	3.5 kg		
Electronic processor unit	2.2 kg		
Power supply unit	1.1 kg		
Total scanner	6.8 kg		
Controls	Available on scanner rear panel or remote cable operation		
Power	ON/OFF toggle switch		
Sensitivity	5 position gain control providing nominally 2°C, 4°C, 8°C, 16°C, 32°C dynamic range displays		
Temperature offset	"Black" level rotary control		
Polarity	Two position control providing displayed temperature inversion (normal - white hot display) (invert - black hot display)		

Detection of oil slicks in the thermal infrared will therefore rely on differences in actual temperature or emissivity. Emissivity differences are relatively fixed, but actual temperature differences may vary due to a host of factors including differences in solar heating, evaporative cooling, thermal conductivity and thermal diffusivity.

Vapour Detector

The vapour detector tested was the Moniteq Oilspills sensor. This is a type of specialized radiometer operating in the near infrared region. It does not detect the oil spill itself but rather the vapour plume that is evaporating from the slick. The oil spill must be of sufficient thickness, areal extent and volatility to permit sufficient evaporation from the slick to produce a detectable vapour plume.

A non-dispersive filter correlation technique is used as the basic measurement technique. The instrument views the upwelling infrared radiation and compares this with the same radiation passed through a target gas cell. The target gas cell contains gas with similar emission/absorption characteristics to the gas which is to be sensed. The background signal and the signal through the target gas cell are measured and electronically balanced. This balance is then upset when a gas with similar absorption/emission characteristics to the target gas is present in the sensor's field of view.

The target gas used in the Oilspills sensor is propane. It was chosen since it has similar absorption/emission characteristics to those gases which emanate from most oil slicks. Propane has a well defined infrared spectra which is distinct from normal atmospheric constituents such as nitrogen, oxygen and water vapour.

The instrument uses a single optical train which is passed through a chopper wheel containing the target gas cell, a neutral filter and a reference blackbody. The detector is cooled by liquid nitrogen and senses in a 0.8 μm waveband centered at 3.4 μm . Since the device operates in the infrared region, oil vapour detection should be possible both day and night. The Oilspills sensor and associated support equipment are shown in Figure 4.

METHODOLOGY

The three sensors were evaluated both under controlled laboratory conditions at the tower tank and under outdoor conditions at the refinery.

Tower Tank Testing

The indoor testing was conducted at the tower tank of the Aquatron facility at Dalhousie University, Halifax, Nova Scotia. The tower tank is silo-shaped deep tank which has a depth of 10.5 m and a diameter of 3.7 m (see Figure 5). Salt water is taken from the ocean and may either be heated or chilled before introduction into the tank. Illumination within the tank was provided by two metal halide lamps.

The sensors were mounted near the top rim of the tank and the tank was partially filled such that the height of the sensors above the water surface was 10.0 m. An access port through the wall of the tower tank was opened permitting various tests to be conducted at the water surface. A retaining boom was positioned on the water surface and used to limit the areal extent of any oil films created. Air temperature could be varied using a heater fan and waves up to 2.5 cm high could be created by positioning a large fan to blow across the water surface. Tests were run using both diesel fuel and

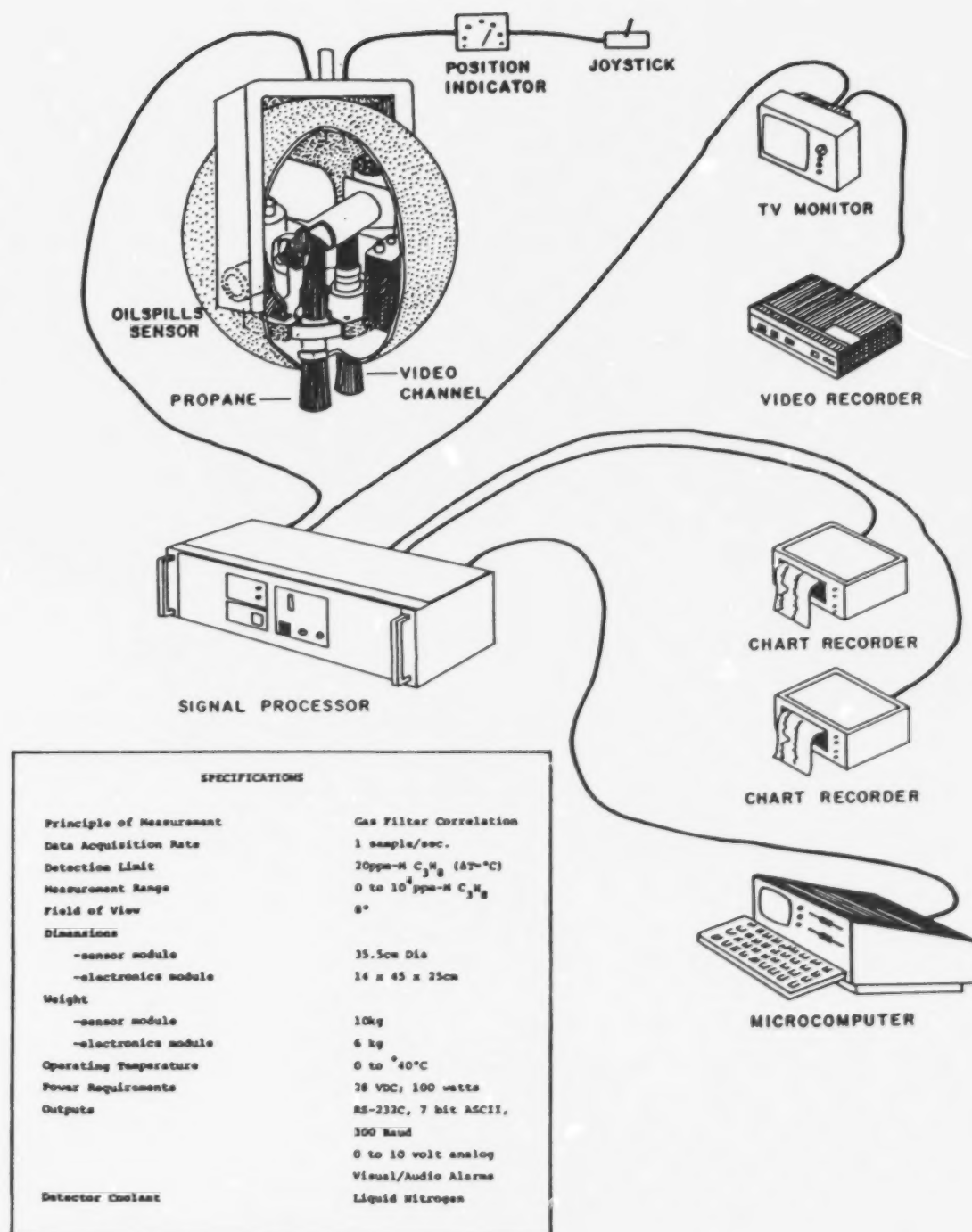


Figure 4. Oilspills Sensor and Associated Electronics
(from Martec 1985)

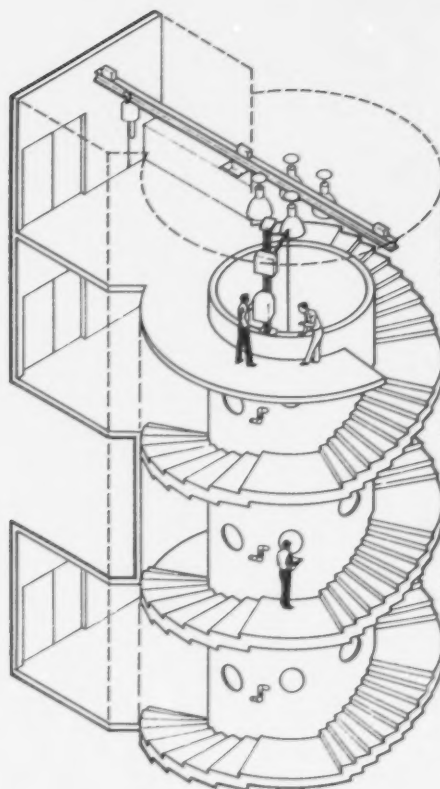


Figure 5. Tower Tank Facility, Dalhousie University

Alberta Sweet Mix crude oil.

Field Testing

The outdoor testing was conducted at Esso Resources Canada Dartmouth refinery, near the outfall from the API separators. The separators are used to treat ballast water, surface runoff from the tank farm, waste oil and excess products during plant upsets. The effluent volume handled varies dramatically depending on plant operation and weather conditions. Some entrainment of oil products into the discharge waters occasionally occurs, but these are handled by a permanent oil-retaining boom which encloses an area of the harbour.

This is a good location for testing oil detection devices since oil films are usually observable inside the boomed area. Experiments were based primarily on whether the sensors could detect the oil under a variety of environmental conditions.

The sensors were mounted on an aerial work platform as shown in Figure 6. The platform had a maximum height above the water of approximately 20 metres at high tide. From the elevated platform, all operating cables were led down to a nearby trailer which housed the instrument controls and data display and storage devices. The aerial platform was positioned such that it was possible to swing the instrument array both inside and outside the boomed area. It was important to have the ability to observe both oiled areas as well as background conditions since some oil detection devices are only able to detect oil by a contrast between the oil and water.

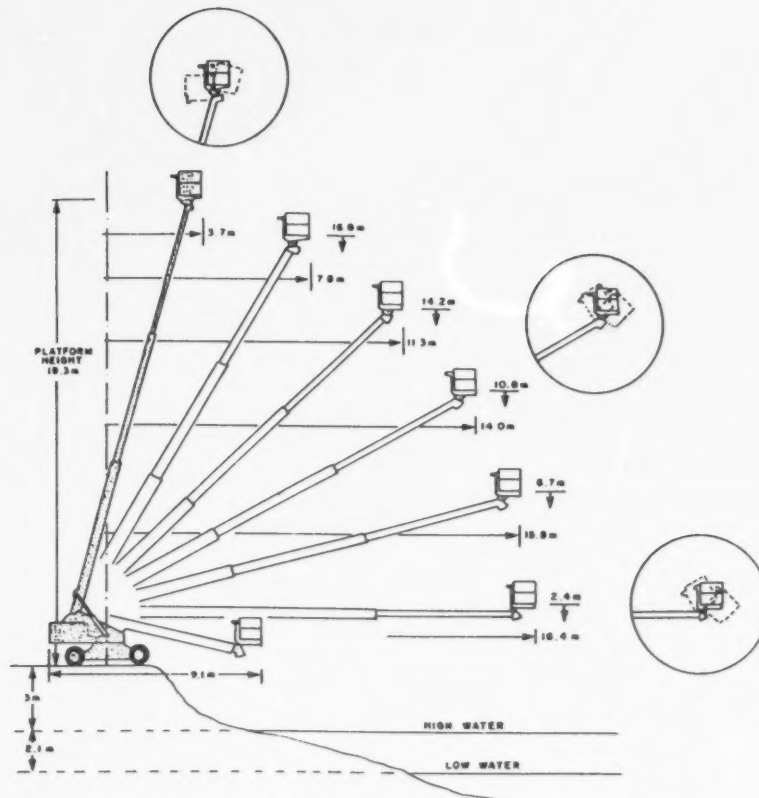


Figure 6. Aerial Work Platform (from Martec 1985)

The field testing at the refinery was broken down into a manual operational phase and an automatic recording phase. Initially the site was manned during normal working hours and a large number of tests with different types and thicknesses of oil were run. The automatic recording phase involved unmanned operation of the sensor array. An automatic event controller was used to switch on the video cassette recorders and trigger the photographic camera at selected intervals. Output was later analysed and used to assess the capabilities of the system at all times, both through the day and night. Oil detection reliability, maintenance requirements and mechanical reliability were the three most important parameters that were assessed during this phase.

TOWER TANK RESULTS

Infrared Oil Film Monitor

The Infrared Oil Film Monitor performed well throughout the tests and did not appear affected by changes in air or water temperatures. The sensor was not affected by variations in background light conditions or minor changes in humidity.

The sensor did show very different detection capabilities for different oil types. It is believed that the spreading characteristics of the different oils was responsible for this. Oils that did not spread effectively under a calm surface environment were not detected except when sufficient oil was present to cover most of the water surface area.

Diesel oil did not spread well but tended to coalesce into lenses of oil which were of considerable thickness. Crude oil and motor oil spread much better and were detected at much lower concentrations. Data on exact oil thicknesses were difficult to obtain because of the variability in slick thickness. From colour plates contained in Fingas et al. (1979), it did appear that if the minimum film thickness over the entire area was approximately 0.3 μm or greater, then a positive response would be recorded. Slick thicknesses less than this tended to have reflection characteristics similar to that of water.

Since the Infrared Oil Film Monitor relies on a reflected signal from the water surface, the initial alignment of receiver optics and lamps is important for correct operation. Alignment involves the adjustment of both the receiver and transmitter until maximum signal levels are obtained. During the tower tank tests, this alignment proceeded very quickly since the calm water surface produced excellent returns. Specially constructed adjustable mounts had been installed on both the receiver and transmitter which permitted quick and accurate alignments.

After this initial setup, signal levels remained very high for the duration of the tests and no other adjustment was necessary. An oscilloscope was set up to monitor signal levels in the 2.5 and 3.1 μm channels simultaneously. A chart recorder was used to monitor the ratio channel output. Ratio channel signal levels varied between 0.25 and 0.5 volts for clean water and 1.5 and 2.0 volts for oil. There appeared to be some correspondence between signal strength and oil film thickness. The manufacturer claims the device has limited ability to differentiate slicks greater than 10 μm thick from thinner slicks.

To test the response of the sensor to oil-on-ice conditions, crushed ice was discharged onto both a clean water surface and an oiled surface. The sensor was not influenced by the ice and gave a strong and correct response to both the oil-on-ice and water-and-ice conditions. Other tests were conducted in which a number of wooden boards were positioned underneath the sensor in an attempt to elicit an incorrect response. The sensor did not produce a false oil signal. Tests by White (1976) with the Wright and Wright sensor have shown that as long as the foreign material is wetted, the sensor response will be that of the wetting medium, either oil or water. This is the result of the sensor only viewing a thin surface layer and not "seeing" into the medium.

To summarize, the Wright and Wright Infrared Oil Film Monitor:

- 1) required a relatively short setup time and no maintenance once installed;
- 2) defined continuous slick and sheen effectively;
- 3) effectively operated at a 10 m height with minimal waves;
- 4) was not influenced by floating ice or debris;
- 5) required that the slick cover greater than about 80% of the surface in the sensed area.

Infrared Imager

Oil has a lower emissivity than water so it should appear cooler than water if both are at the same temperature. During the tower tank tests, a variety of air temperatures, water temperatures, lighting configurations and oil types and thicknesses were tried. Oil films as thin as 0.4 μm were clearly

observable and at all times the oil films had a higher apparent temperature than the water.

The only suitable hypothesis that would explain these results in that the oil films were inhibiting evaporative cooling of the water surface. Horvath et al. (1970, from O'Neil et al., 1983) has collected measurements of attenuation coefficients of a number of crude oils in the wavelength region 8.5 to 12.5 μm and has found them to be near 0.005/ μm . These data indicate that a 320 μm thick oil layer is required for 80% of the thermal radiation to be emitted from the oil and 20% from the underlying water. Therefore, for the thin oil films created in the tower tank, the IR imager was detecting primarily the water beneath the oil rather than the oil film itself. Oil films were detected because they reduced the evaporative cooling of the water beneath them. Emissivity differences or radiative heating may be considered to be secondary factors.

Oilspills Sensor

The Oilspills sensor as used during the tower tank tests was operated from a height of 10 metres above the water surface pointed directly downwards. Real-time output of the gas and radiance signals was available from a television monitor in both graphical and numerical format. The data was also logged onto diskette which permitted more extensive data manipulation using a micro-computer at a later time.

Results from the Oilspills sensor were not encouraging. A large number of tests with crude, diesel and motor oil were conducted over a variety of air-water temperature regimes. The Oilspills sensor failed to give a positive response to oil vapour in any of these situations. At one point, a heater gun was even positioned to blow across a pan of diesel oil to induce evaporation. Although diesel vapours were clearly evident to the nose, the Oilspills sensor failed to give a response.

Large variations in signal levels were almost always present and this made interpretation very difficult. Large variations in signal were especially evident during instrument warm-up which lasted for approximately 15 minutes. Once instrument warm-up had occurred, it became clearly evident that changes in the radiance signal were affecting the gas channel output.

The only positive response to hydrocarbon vapour occurred when small quantities of propane were introduced into the tank. The response was immediate but relatively short lived, lasting for approximately one minute.

FIELD TEST RESULTS

The field testing was conducted over a two week period at the Dartmouth refinery. It included both a manual operational phase and an automatic recording phase. The manual operational phase involved the intensive operation of all sensors in an attempt to determine the operational parameters and oil detection limits of each unit under a wide variety of environmental and illumination conditions. The automatic phase involved the unmanned operation of the sensors. The automatic control box was used to switch on the relevant video recorders and take pictures at selected intervals. Output could later be analysed and used to assess the suitability of this type of system for offshore deployment. Maintenance requirements, mechanical reliability and oil detection reliability were the three most important parameters that were assessed during this phase.

Infrared Oil Film Monitor

The primary objective in testing the Infrared Oil Film Monitor was to

evaluate its capabilities under wavy conditions and at operating heights greater than 10 metres. The approach taken was to operate the sensor continuously from a height of 15 or 20 metres while noting surface wave conditions and the presence or absence of oil films.

The instrument was found to be mechanically reliable throughout the testing except for one occasion when condensation on the inside of the detector window produced a false response. The oil film monitor performed well at a height of 15 metres and gave a positive oil response in every situation when an oil film was present beneath the sensor. Voltage levels for clear water ranged between 0.1 and 0.5 volts and oil films produced voltages from 0.5 to 2.0. Wave action was effective in spreading different types of oil and as a result, all types of oil were detected equally well. Increasing wave action (up to 0.3 m wave height) tended to increase background signal levels but at no time did the clear water signal level increase past 0.5 volts. The only instances where incorrect oil responses occurred was when the sensor was incorrectly aligned. In this situation, signal levels went off scale, and it was obvious the sensor was operating incorrectly.

When operating the sensor from a 20 metre elevation, oil was detected in most situations, however the overall operation of the sensor and interpretation of data was more difficult. Correct setup of the sensor at the 20 metre elevation was much more important than at the 15 m operating height. Both the alignment of the receiver and transmitter and levelling operations required considerable time. Background voltages from the ratio channel varied between 1.0 and 3.0 and were highly dependent on the water surface conditions. Swell conditions were found to produce the highest background voltages from the ratio channel, presumably since the reflected signal was out of range of the receiver for a large proportion of the time. Poor signal return results in a high ratio since the denominator of the term becomes very small. Integration over a large number of readings results in high background signals. Operation of the sensor in chop produced lower background signals and better responses to oil, presumably since with chop, there are a greater number of reflecting wave facets normal to the optical axis of the sensor.

Thermal Imager

The Thermal Imager proved to be mechanically reliable throughout the tests and was not affected by changes in atmospheric temperature or humidity. Penetration of fog and rain was good, but heavy snow tended to obscure image detail. The best conditions for oil detection with the Thermal Imager were clear skies, minimal wind and wave action and thick oil films. Daytime observations during these conditions showed the oil as a continuous warm area. Solar heating of the oil caused its temperature to rise above that of the surrounding water.

Detection in the thermal infrared was found to be quite sensitive to surface conditions. A chop on the water surface would break up thin oil films and induce mixing of warm surface and cool subsurface waters. Imagery taken during these conditions exhibited great contrast with many rapidly moving and changing features that were impossible to interpret or quantify.

The configuration of the imager, as tested was not well suited for long term deployment. The high pressure air bottle required recharging every 8 hours with ultra-pure air. The telescopic lens permitted only limited areal coverage. Since oil is detected by determining a contrast in an image, the areal coverage of the sensor should include both the oil film and a clean water surface. With the telescope used, often clean water areas or oiled areas would completely cover the sensor's field of view. In these situations,

it was not possible to define the surface as either oil or water.

Oil detection at night with the Thermal Imager was not as effective as in the daytime due to a reduced thermal contrast. Oil discharged from the separators was observed several times at night as warm areas but they were difficult to verify at night. Effective sampling and visual verification of the oil films was difficult with the nighttime lighting available at the site.

The thermal IR imagery was able to provide some definition of oil films both day and night but was unable to positively identify the oil. Although surface oil was always seen as warmer than the clean water, the contrast between the two was often not great. Other effects are capable of producing larger temperature contrasts which confused the interpretation of the imagery. An additional means of verification is required before oil can be positively identified.

The video output of the sensor did not lend itself to an alarm function for remote operations.

Oilspills Sensor

The sensor was found to be mechanically reliable except for one instance during extremely cold weather when start-up resulted in a thrown circuit breaker. The sensor, electronics and data storage and display devices require considerable space and numerous cables. Real-time interpretation directly from the television monitor is difficult since only 8 data points are shown. Effective data analysis required storage of raw data on diskette which was then outputted as computer plots. The dewar containing liquid nitrogen requires re-filling at 3-4 hour intervals which was found to be time consuming and logistically difficult.

The Oilspills sensor did not respond to ambient oil levels inside the boomed area but this was not surprising considering the non-volatile nature of the oil discharged from the separators. A number of intentional oil releases were conducted with crude, diesel and even gasoline directly below the sensor but no positive response was registered. A variety of operating heights ranging from 5 to 15 metres were used but none appeared to improve oil detectability.

If the Oilspills sensor responded at all to the oil films during the outdoor tests, it was within the noise level of the instrument. Background gas signal level contained considered noise and longer term variations in signal levels corresponded quite closely with changes in radiance. The instrument did detect propane but only from a one metre operating height which indicates the limited sensitivity of this unit.

CONCLUSIONS

Wright and Wright Infrared Oil Film Monitor

The sensor was found to be completely effective when operating from a height of 15 metres. A low baseline over clean water was maintained at all times. Oil films produced a sudden and significant response sufficient to trigger an alarm. The sensor alarmed on very thin films but did require that the oil film be fairly continuous.

When operating from a 20 metre height over clean water, the baseline was affected by surface wave conditions. The larger the waves, the higher the background signal. Response to oil above the background condition appeared to be in rough proportion to the magnitude of the background signal already present. Although it was obvious from the chart recorder data when an oil film had occurred, a preset alarm level could not have been selected and expected

to work under all surface wave conditions.

The Wright and Wright monitor was the only sensor tested which was specifically designed for continued surveillance of oil films. As such, it already possessed many of the features that would be required by an offshore monitor, such as low maintenance requirements and an alarm capability.

Barr and Stroud Thermal Imager

In most situations, the Thermal Imager had sufficient sensitivity to detect apparent temperature differences between the oil and water. However, positive identification of slicks was often difficult. Oil may appear either warmer or cooler than the water, depending on the environmental conditions present at the time of the imagery. Mixing of surface and subsurface water of different temperatures by wave action, acts to further complicate the interpretation of the imagery. Additional information is usually required before positive identification of the oil may occur. For these reasons, simple alarm monitoring in the presence of oil slicks will be a very difficult task to accomplish with the Thermal Imager.

Oilspills

The Oilspills sensor could not positively identify oil slicks. There were two fundamental problems: excessive background noise and low sensitivity. The instrument required a considerable warm-up period and even after warm-up, large swings in signal levels occurred. Changes in radiance resulted in sudden and large changes in the gas signal level. Interpretation was very difficult due to this high and variable background, compounded by the fact that oil vapours may produce either an increase or decrease in gas signal level.

Furthermore, the instrument was not sensitive to vapours emanating from oil spills. Spills of both diesel and crude were tested both in the field and under controlled conditions. In the tower tank, concentrated oil vapours were created, especially when a heater fan was used to induce oil evaporation. Even this situation failed to produce a significant and identifiable response.

RECOMMENDATIONS

Further testing of the Barr and Stroud Thermal Imager is not recommended. Although the infrared imager can define oil films under most conditions, a means of verification is almost always required. Furthermore, design of an effective automatic alarm system utilizing the video output from this device would be difficult and probably prove unreliable. The Barr and Stroud Infrared Imager should continue to be used in oil surveillance sorties, but not relied on for continuous oil monitoring.

The Oilspills sensor in the present format is not able to detect oil films on the water surface. The sensor should be re-evaluated with effort focused on determining exactly what constituents of an oil slick the sensor can detect, and whether these constituents are evaporating from oil slicks in sufficient quantities to be detected. Other considerations should include reducing the effects of radiance changes on the gas channel output, and the design of a real-time plotting program for the microcomputer. Development of an effective operators manual detailing the exact operating theory of the sensor is considered imperative. A modified Oilspills sensor must show adequate results during laboratory tests before any further outdoor testing is considered.

The Wright and Wright Infrared Oil Film Monitor does warrant further evaluation. The recommended study would involve short term deployment of

the instrument at an offshore platform, during which time a number of controlled spills with non-toxic oils (e.g., vegetable oil) would be undertaken. Design and construction of a suitable housing for offshore deployment would be necessary but not difficult. Digital processing of the data should be considered since it would allow for compensation for variations in water surface conditions. A smaller field of view combined with more highly focused lamps may permit operation at higher elevations and should also be considered.

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ASPECTS OF THE DETECTION OF OIL UNDER SEA ICE
USING RADAR METHODS

by

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INTRODUCTION

The purpose of this study is to examine the possibility of detecting oil under sea ice using an airborne radar technique. The positive identification of oil is likely to be frustrated by the scattering of radar signals from the top surface and by air bubbles and brine inclusions as well as by the Joule losses associated with the salinity within the body of the ice. To minimise these effects it is desirable to operate the radar at frequencies that are somewhat lower than is usual, say a few hundred MHz. In this work, attention is confined to the range 100 MHz to 1 GHz. However the spatial resolution of such a radar is likely to be quite poor. For example, with an antenna diameter of 1 m and a wavelength of 1 m, the beam width of a conventional radar is about 1 rad. This severely reduces the quantity of data that may be gathered from an area in which there may be oil pools of a few metres in diameter and over which it may be important to resolve spatial variations of similar size. Problems are compounded by the fact that there appears to be little to distinguish signals from the lower boundary of the ice in the presence or absence of oil. Oil has a relative permittivity a little greater than 2, whilst according to data collected by Kim (1984), the real part of the relative permittivity of ice ranges between 2.5 and 4.0. For comparison, the permittivity of sea water is about 80. Thus it appears that a simple detection system would have to rely mainly on the changes in the character of the water surface and its scattering properties: it would be expected that the surface would be flatter in the presence of oil.

To utilise the changes in the lower surface a much better resolution than that yielded by the conventional antenna is required: cell sizes of 1m or less are needed. These can be obtained, at least in principle, by employing the techniques of synthetic aperture radar (SAR). A description of these is given for example by Hovanessian (1980).

It will be demonstrated that the observation of changes in the lower surface is not very promising. A more sophisticated method may be to exploit the phase changes that occur when em radiation is reflected at a dielectric interface. In the present case the permittivity of oil is less than that of ice whilst that of water is greater. Therefore there will be differences in the phases of the signals scattered with horizontal-horizontal or vertical-vertical polarisation from these two types of interface and these differences in the returned signal could provide a "feature" to strongly identify the presence of oil. Unfortunately there appear to be some technological problems in combining the SAR principles with the measurement of relative phase. These are primarily associated with the antenna design, which requires a high degree of isolation with respect to polarisation as well as a large bandwidth (determined by the range resolution).

A typical SAR arrangement is shown in figure 1. The range direction is perpendicular to the aircraft track and, along track (the azimuthal direction), spatial information is obtained from the Doppler shifts by applying a matched filter to the complex received signal.

Because of the difficulties to be expected, it is prudent to examine first the simple detection of oil without regard to the extent or depth of the pollutant. The radar signals would be fed to a classifier which would attempt to provide as output one of the two classes "oil" or "no oil".

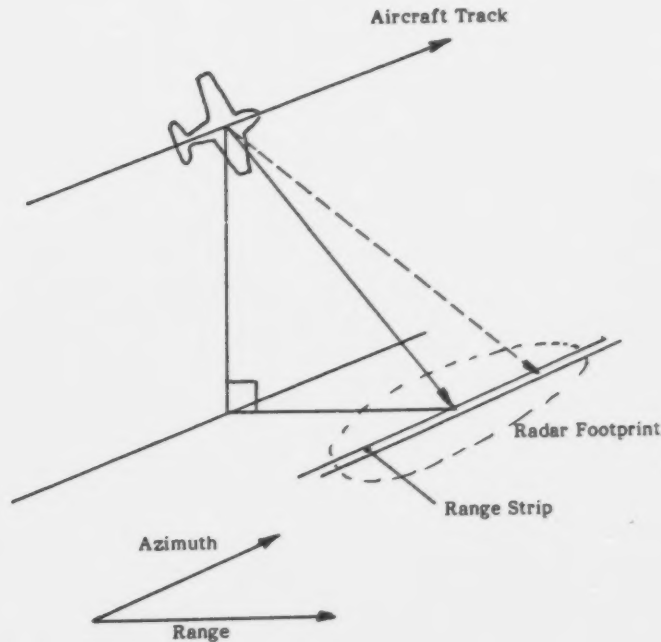


Figure 1
Airborne SAR with side-looking antenna:
azimuthal data from Doppler information

THE CLASSIFIER

Pattern recognition has received great attention over the last 15 years and a good review of the field has been made by Bow (1984). The two-class problem has received particular attention as it is the simplest. The signal to be

classified (for example a record in space or time) is conveniently visualised as a position vector in a hyperspace, typically with a large number of dimensions. A hypersurface is imagined to separate two regions of the hypervolume each of which contains primarily one class of signals. It is to be expected that random noise will occasionally cause some signals to fall on the wrong side of the boundary and cause a misclassification. The task of classification is to find the best "rule vector" to represent a separation plane: this vector can be regarded as a normal to the plane.

A popular method is to find a transformation or rotation matrix which tends to concentrate the information into a few of the signal vector components. This is the Karhunen-Loeve or eigenvector expansion in which the covariance matrix is diagonalised. The vector corresponding to the largest eigenvalue of the covariance defines a direction in the hypervolume along which the variation is in some sense a maximum. Classification is achieved by finding the scalar product of a signal vector with the rule vector and, if it is arranged for the class separation plane to intersect the origin, the sign of the result gives the class.

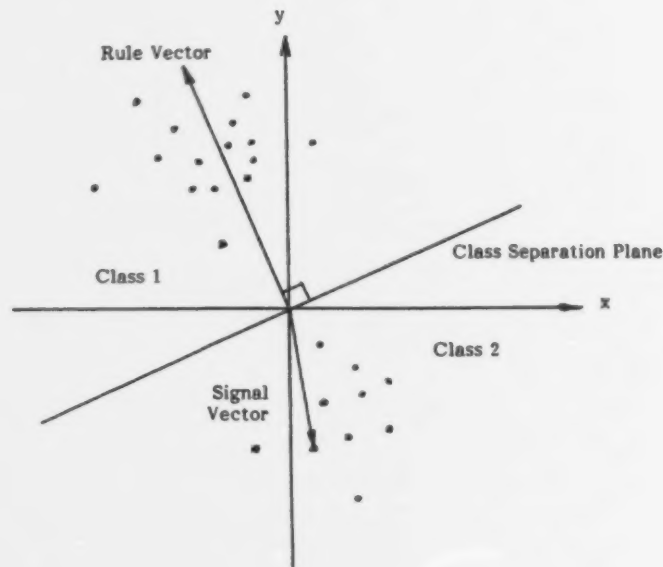


Figure 2
A classification scheme in two-dimensions

The K-L transformation is not optimal, since a considerable amount of information resides in the other transformed vector components. Another method is due to Foley and Sammon (1975); a rule vector is sought but here a vector

which maximises the ratio of "between class mean" to "within class variation" is found. This has better discrimination potential. Again the scalar product of the rule vector with the signal vector is determined. The general idea is illustrated in figure 2. In many situations the K-L and the Foley Sammon vectors are not very different.

In the present study we are concerned with the detection of pools of oil under the ice. These do not lie in any predetermined spatial position with respect to the radar but will be scattered in some random fashion. Therefore an information preserving transformation should be made to yield a signal which is invariant under translation. The appropriate transformation is the Fourier transform: in particular for a stationary Gaussian signal, no information is carried by the phase and the pertinent information is contained in the spectral density components. This spectral density can be used as the input to the classifier. There will be a loss of information in the general case but hopefully this will be quite small.

It should be emphasised that the application of additional transformations will almost certainly not result in a better classifier performance but rather the reverse because information will usually be lost.

Since the effect of oil on the signals is difficult to determine analytically, the discrimination vector must be found either from real or simulated data. There is an advantage to the use of a self-learning algorithm in that a continuous updating and refinement of the rule vector can be made. In the terminology of Artificial Intelligence or "Expert Systems" the classifier would be of the "non-parametric decision theoretic" type. Training of the classifier consists of presenting signal vectors from known situations for classification. If the classifier predicts the correct result, nothing is changed. However, if it makes an incorrect prediction, the rule vector is modified by either adding the signal vector or subtracting it, depending on the true class. During a training session the reliability of the system, expressed as the fraction of correct predictions in a given number of trials, approaches some asymptotic value which is a function of the S/N ratio. A simple classifier along these lines has been described by Naylor (1983) and the method has recently been successfully applied to the classification of radar images of ship superstructures by Tunaley et al (1986).

The S/N ratio is critical to the classifier performance and it is desirable to employ averaging to reduce the scatter around the class means. This could be achieved by averaging the spectra from several sets of data at different radar ranges. If H-H and V-V polarisations are employed and the extra phase information used to augment the signal vector, the effect will be to increase the mean distance between class means.

In view of the large number of imponderables, a simulation of the radar signals and a classifier is a good way of testing the feasibility of a system.

THE MODEL

A summary of radar backscatter from sea ice has been made by Ulaby et al

(1986). The main aim of previous work seems to have been the classification of ice types. Theories of scattering from ice have been proposed by Parashar et al (1978) and Kim (1984). Kim's theory appears to explain winter scattering from thick first year and multiyear ice quite well and also has the advantage that it is simple. Experimental verification was made at frequencies usually above 2 GHz. The theory is based on a model in which surface scattering and volume scattering from spherical inclusions are considered; the radar backscatter coefficient as a function of the angle of incidence, θ , takes the form:

$$\sigma^0(\theta) = \sigma_s^0(\theta) + Y^2(\theta)(\sigma_v^0(\theta') + \sigma_g^0(\theta')/L^2(\theta'))$$

where σ_s^0 is the coefficient for the top surface, σ_v^0 is the volume coefficient for the ice, σ_g^0 is the coefficient for the bottom surface, Y is the power transmission coefficient across the upper surface, L is the one-way loss factor through the layer of ice and θ' is the angle of refraction in the ice.

At lower frequencies this type of model is likely to become a better approximation to reality. As the wavelength increases, the scatter from small inclusions will be described more accurately by the Rayleigh scattering theory. The amount of scatter by the inclusions will also fall making it unnecessary to introduce radiative transfer theory. However the assumption of spherical shaped inclusions is a potential problem. For example the brine inclusions tend to be better represented by prolate ellipsoidal spheroids and, if there is a significant component of the incident electric field parallel to the long axis of the spheroid, a greatly enhanced scattering can result. This could affect the variation of scattering coefficient as a function of angle of incidence. The type of polarisation would also be a factor. The scattering of em waves by spheroids has been treated for example by Tunaley and Moorcroft (1985): the results are summarised in the appendix. For typical complex permittivities of sea ice and brine, it is shown that, with axial ratios of up to 20, enhancements in scattering coefficient of up to 400 can occur. Fortunately the spheroids will usually be aligned more or less vertically and, considering that the angle of refraction in ice is usually small, the geometry is not conducive to such extreme factors. However it should not be surprising if significant differences are observed between signals arising from volume scattering with H-H and V-V polarisations.

The surface scattering contribution can be handled using the methods of Rice (1951), which can be understood in terms of the Bragg mechanism. At the higher frequencies in the GHz range, absorption is likely to make the reflection from the bottom surface quite small: the two-way absorption at 1GHz in even multiyear ice is typically 10 dB/m at temperatures just below freezing. Thus the bottom does not play a dominant role in Kim's theory and simple reflection from the bottom followed by forward scattering at the top is not considered explicitly. This may be important at the lower frequencies and has been discussed by Tunaley (1985).

The back-scattering coefficient for a slightly rough dielectric interface is of the form:

$$\sigma_s^0 = 4k^4 \cos^4 \theta \alpha_{pp} P(2k \sin \theta, 0)/\pi$$

where k is the em wavenumber in the incident medium, α_{pp} is a coefficient depending on the polarisation, the permittivities of the media and is a weak (usually) function of the angle of incidence. P is the two-dimensional power spectral density of the surface height variations. Kim employed a surface model characterised by a standard deviation in the height of the order of 1 cm and a correlation length, l , of the order of 10 cm. A simple stochastic model, such as that presented by Tunaley (1985), indicates that the scattering coefficient appropriate to the top surface would be approximately proportional to k for small wavelengths such that $(2kl \sin \theta) \gg 1$. This appears to be consistent with data assembled by Kim (1984) and reproduced by Ulaby et al (1986). However, in the UHF range and with the surface characteristics assumed by Kim, the model predicts a much greater dependence on k , possibly as great as k^4 . However, on these larger spatial scales the simple stochastic model is a little suspect: Ulaby et al (1986) point out that natural surfaces possess a large range of correlation lengths. More general models have been discussed by Tunaley and Moorcroft (1985) and are based on fractal surfaces an example of which is shown in figure 3.

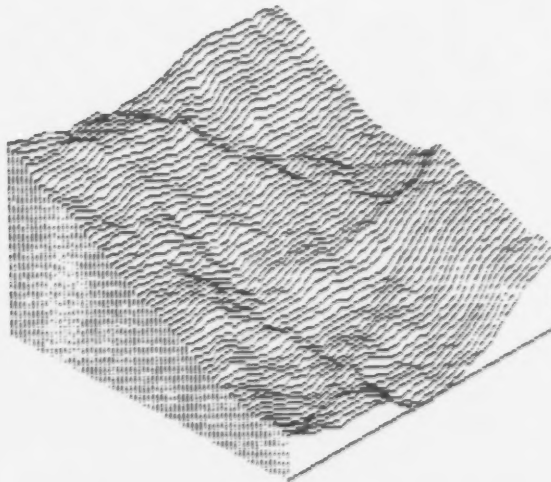


Figure 3
Example of a fractal surface - scales are arbitrary

The volume scattering coefficient can be expressed in terms of the cross section for a single scatterer. In the case of a spherical bubble, the latter is given by

$$\sigma_b = k^4 a^6 |(m^2 - 1)/(m^2 + 2)|^2$$

where k is now the wavenumber in the embedding medium, a is the sphere radius and m is the ratio of complex permittivities (internal over external). Ulaby et al (1986) show that

$$\sigma_v^0(\theta^-) = N\sigma_b \cos\theta^-(1 - L^{-2}(\theta^-))/(2\kappa)$$

where κ is the extinction coefficient, related to the loss factor and the thickness of the layer containing bubbles, d , by

$$L = \exp(\kappa d \sec\theta)$$

and N is the number density of the bubbles, all of identical size. The factor of k^4 in the coefficient indicates that scattering is likely to be small at UHF but will tend to dominate at sufficiently high frequencies. For first year ice, which does not contain many inclusions, Ulaby et al (1986) present curves showing that the volume and surface scattering contributions become equivalent at a frequency of the order of 10 GHz even for a "smooth" top surface. For multiyear ice with a "smooth" surface the cross-over frequency may be lower than 4 GHz. However, at the frequencies considered here for the detection of oil, volume scattering is not likely to be the dominant contribution. Noting that the contribution of Rayleigh scattering from spheres is not a strong function of the angle of incidence, this is quite important as it means that low depression angles can be utilised to effect a gain in the ratio of bottom to top scattering at low depression angles as described by Tunaley (1985).

Clearly the volume scattering coefficient is critically dependent on the radius of the inclusions. In practice the distribution of sizes will be very important but this is not known. Thus experimental data must be utilised to estimate typical coefficients: we can refer to Onstott et al (1977 and 1981) or Gray et al (1982). Although this data is for the higher frequency range, it is more suitable for estimating volume scattering especially for multiyear ice, where it is sure to dominate. However a complicating effect is the reduction of the absorption at lower frequencies, which increases the volume in which scatterers may effectively contribute to this type of scattering. Thus models of salinity are important: an appropriate bilinear model may be developed using the expressions given by Moorcroft and Tunaley (1985), which relates the real and imaginary parts of the dielectric constant to the brine volume and the radio frequency.

The simulation model requires both upper and lower surfaces which, because of hydrodynamic and thermal effects, cannot be independent. For example a large hillock on the upper surface will generally be counterbalanced by an even larger one on the lower surface but of the opposite sign. If the latter is not present, hydrostatic forces are liable to shear the ice sheet. Thus a negative correlation must exist in this situation, which will be typical at the larger scales. On the other hand, a varying thickness of snow, such as may occur in windrows, produces a variation in the thermal conductance of the snow layer. A thick blanket of snow may inhibit the formation of new ice on the under surface and a positive correlation could be the result. Whilst it is possible to implement quite complicated models in a simulation (typically involving a correlation that is a function of scale), we propose to limit consideration to a single (either positive or negative) correlation on the basis that the main

effects in scattering are due to variations on scales near the Bragg wavelength. The model can be generated by constructing two independent surfaces and then transforming the heights at each point according to some matrix:

$$\begin{pmatrix} h_u' \\ h_l' \end{pmatrix} = \begin{pmatrix} \cos \gamma & \sin \gamma \\ \sin \gamma & \cos \gamma \end{pmatrix} \begin{pmatrix} h_u \\ h_l \end{pmatrix}$$

It can easily be verified that the correlation matrix of the primed heights is

$$C = \begin{pmatrix} 1 & \sin 2\gamma \\ \sin 2\gamma & 1 \end{pmatrix}$$

so that either positive or negative correlations may be obtained by an appropriate choice of γ . An example of a vertical cut through a layer of ice is shown in figure 4. The surfaces are fractal surfaces obtained by using an algorithm developed by Goodchild (1985). The average ice thickness must be specified and, in general, provision must be made to handle the case when the surfaces intersect: this could be interpreted as a lead or polynya).

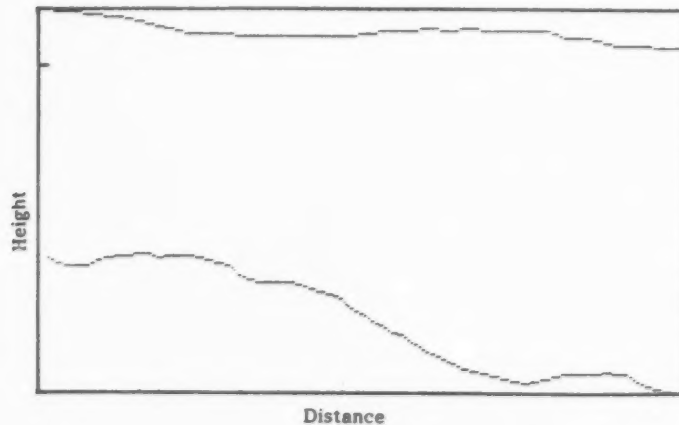


Figure 4
Example of simulated ice profile

The radiowave scattering simulation must be handled in a way that preserves the phase of the signals. A Kirchhoff approach could be adopted to avoid having to satisfy boundary conditions explicitly. (This method just takes into account the ray path lengths.) Though it is known to be inadequate for dielectric interfaces, coefficients can be "borrowed" from the more exact theory of Rice, for example. For the inclusions the phase from each scatterer can be treated as completely random. Again though not strictly valid, this should represent a

slightly worse case than reality in terms of the unwanted noise introduced by the air bubbles and brine pockets. Taking into account absorption, as noted above, calculations of the total scattering intensity from centres located within one radar resolution cell can be made ahead of time to reduce computational effort. This would probably be based on the assumption that the scattering amplitudes are statistically stationary with respect to position. Thus the complex amplitudes could be visualised as vectors in the Argand diagram having a two-dimensional normal distribution.

EXPECTED RESULTS

The key to the successful detection of oil is the operation under conditions where, in the signal space (or a transformed version of it), the mean distance between classes is much larger than the "within class" variation. However ice is notoriously variable and, unless some classification of ice type can be made beforehand, this is sure to create a large contribution to the "within class" noise. The other problem is the nature of processed SAR image intensities. These also contain a large noise component, characteristic of coherent systems, called "speckle" from its appearance in laser imagery. Speckle will be generated automatically in the proposed simulation and should be reduced by averaging in both azimuth and range.

Speckle is often modelled as multiplicative noise and drastically reduces the information carried by the intensity of one resolution cell: in this application it is more or less equivalent to a S/N ratio of 1 in the intensity. Thus, to obtain a S/N ratio of say 100 in a derived parameter (such as the projection of the signal vector on the rule vector), it is necessary to average at least 10,000 signals from independent resolution cells. A loss of 10dB due to absorption would reduce the S/N ratio for signals from the under surface to 10. Therefore, for the detection of oil spills of horizontal extent much less than 1 km by 1 km, the simple method of looking for changes in the bottom topography is at best marginal.

An improvement might involve the use of a dual polarisation SAR with a phase measurement between H-H and V-V signals. In this case it is desirable to investigate and include in the simulation cross-polarisation effects at the interfaces. However the main problem may well be the antenna isolation with respect to polarisation when operating at a few hundred MHz. Isolation has been addressed by Claassen and Fung (1977) and by Blanchard and Jean (1983). Poor isolation is likely to occur in directions away from the principal direction of the antenna (boresight) and this is mainly due to induced currents and reradiation from adjacent conducting structures such as supports and mounts and the aircraft skin. At low frequencies such objects tend to be electrically closer to the antenna and their effects more acute. The latter authors give an example of a parabolic antenna in which there is typically much less than 10dB isolation.

A final conclusion on the possibility of detecting oil under sea ice must await the simulation.

ACKNOWLEDGEMENT

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APPENDIX

SCATTERING FROM SPHEROIDS

The Rayleigh scattering from ellipsoidal spheroids has been treated for example by Tunaley and Moorcroft (1985). This is not an original derivation but correct results seem to be difficult to find. The geometry is shown in figure 5, where the axis of revolution is parallel to the z-axis. It is possible to show that the cross-sections for the scattered wave polarisation in the ζ or η directions are given by

$$\sigma_{s\zeta} = (3/(4\pi))^2 k^4 V^2 L_t^2 g_1^2$$

$$\sigma_{s\eta} = (3/(4\pi))^2 k^4 V^2 (L_1^2 g_2^2 + L_t^2 g_3^2 + 2L_1 L_t g_2 g_3 \cos(\psi_1 - \psi_t))$$

where V is the volume of the spheroid and

$$g_1 = \sin\beta \cos\phi_s + \cos\beta \cos\theta_i \sin\phi_s$$

$$g_2 = \cos\beta \sin\theta_i \sin\phi_s$$

$$g_3 = \cos\theta_s (\cos\beta \cos\theta_i \cos\phi_s - \sin\beta \sin\phi_s)$$

The quantities L and ψ are related to the complex quantity, α , expressed in a polar form:

$$\alpha_{1,t} = 3\varepsilon V((m^2 - 1)/(3 + (m^2 - 1)Q_{1,t}))$$

where ε is the permittivity of the external medium, m is the ratio of the internal to external permittivities and

$$Q_1 = 3((1 - e^2)/e^2)(\ln((1 + e)/(1 - e))/2e - 1)$$

$$Q_t = (3 - Q_1)/2$$

e is the eccentricity of the spheroid:

$$e = ((a^2 - b^2)/a^2)^{1/2}$$

and

$$V = 4\pi ab^2/3.$$

Also the complex α is regarded as

$$\alpha = (3\varepsilon V)L \exp(-i\psi).$$

For example, for backscattering, the angles θ_i and θ_s are equal and ϕ_s is zero. With horizontal polarisation $\beta = 90$ degrees so that

$$\sigma_s = (3/(4\pi))^2 k^4 V^2 L_t^2$$

In the case of a sphere $Q_{1,t}=1$, so that

$$\alpha = 3\varepsilon V((m^2-1)/(m^2+2))$$

which yields the scattering cross-section quoted earlier in the main text.

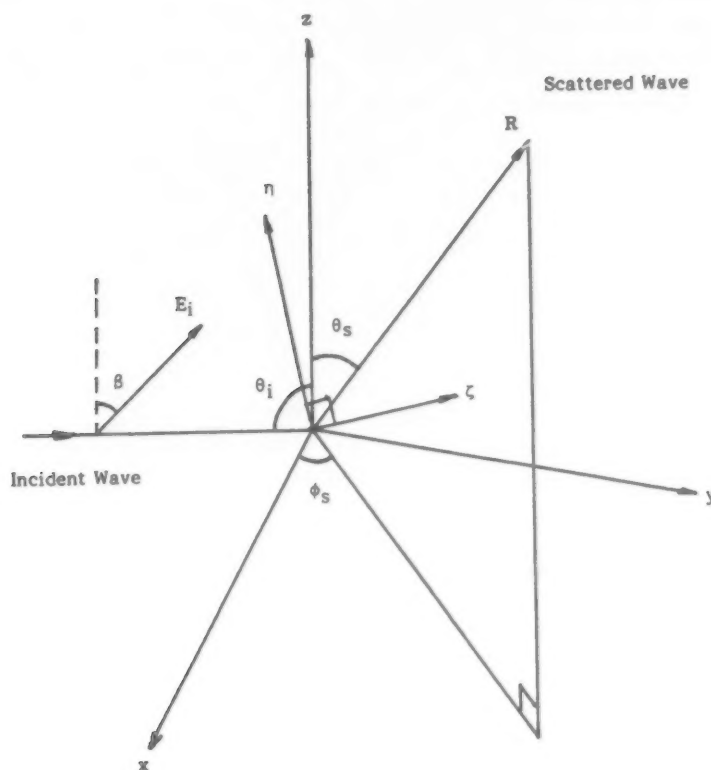


Figure 5

Scattering geometry. The incident ray lies in the x - z plane and β is the angle between this plane and the electric field vector. The ζ axis lies in the x - y plane and the η axis is normal to both it and R .

THE DETECTION OF OIL UNDER ICE BY ULTRASOUND USING MULTIPLE ELEMENT PHASED ARRAYS

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ABSTRACT

In previous contributions to the AMOP conferences we have described an ultrasonic method for detecting oil trapped under arctic ice. Most recently an automated system has been described using a multiple element phased array receiver. This paper describes a prototype field instrument for use in arctic conditions. Advancements in the construction and signal processing of the array are described, and results of field trials are given.

INTRODUCTION

In previous papers^{1,2,3,4,5} it has been demonstrated that the detection of oil layers under ice by the reflection of ultrasound is a practical technique. Briefly, the technique uses pulsed ultrasound directed obliquely at the undersurface of the ice. The presence or absence of oil is determined by the amplitude ratio of the reflected and mode converted waves received at the upper surface (figure 1).

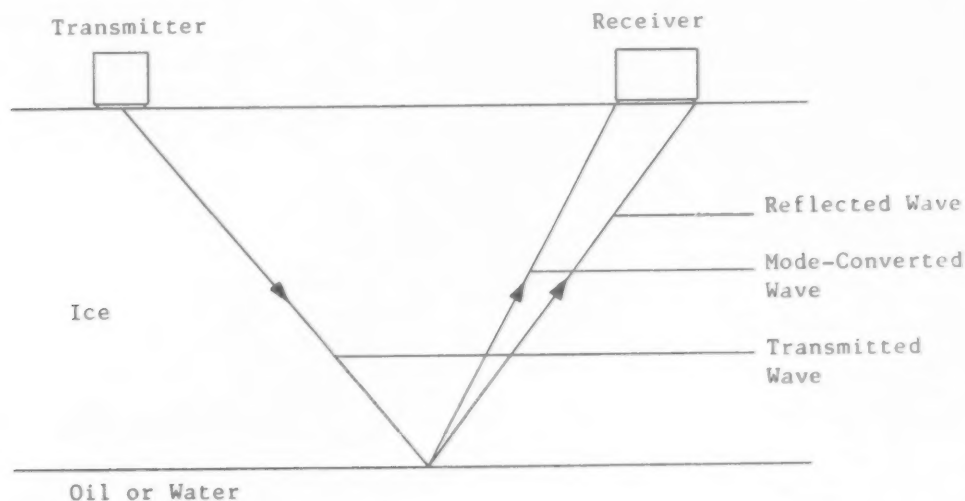


Figure 1. Geometry of Ultrasonic reflection system for detection of oil under ice.

The primary impediment to the realization of a reliable field apparatus has been the difficulty of extracting the two relevant pulses from a background of reverberant and scattered ultrasound. The unwanted signals consist of reflected, mode converted and scattered waves from inhomogeneities in the ice such as cracks, brine channels and growth layer boundaries. In recent publications^{6,7} we have described a computerized instrument which used a phased array receiver for improvement in signal to noise ratio. The phased array allows directional discrimination of signals, which when combined with time-base discrimination allows rejection of most of the reverberation noise. While this earlier instrument gave good results, it was too bulky for arctic use. Recent work has concentrated on producing a rugged, portable field instrument, and in producing a phased array of more advanced design.

PHASED ARRAY SIGNAL ANALYSIS

An acoustical receiving array is simply a number of receiving transducers, arranged in some configuration, whose individual outputs are summed to produce a net output signal⁸. If a signal arrives in phase at all elements, the sum will have the maximum amplitude, whereas a signal arriving in some other direction will produce individual signals that are not in phase, and the summed amplitude will be reduced accordingly. The direction of maximum response is known as the main lobe of the array. In addition, most arrays will have secondary maxima which are called sidelobes. To achieve the best resolution, given practical restrictions on the number of elements and the overall dimensions, an array must have a satisfactorily narrow main lobe and sidelobes must be weak or absent.

Before the signals from individual arrays are summed, they can be time-delayed by varying amounts according to their positions. This is equivalent to physically repositioning them, and in this way the main lobe of the array can be dynamically steered in any desired direction. While beam steering employs linear variation of time delay with element position, higher-order delays can be used to focus the array to 'look' at a small area at a particular range.

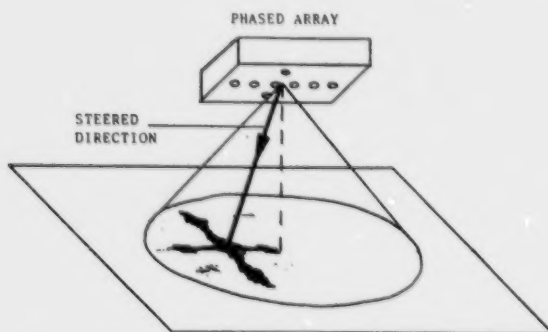


Figure 2. Geometry used for mapping phased array sensitivity patterns. Circle represents off-vertical angle of 45° .

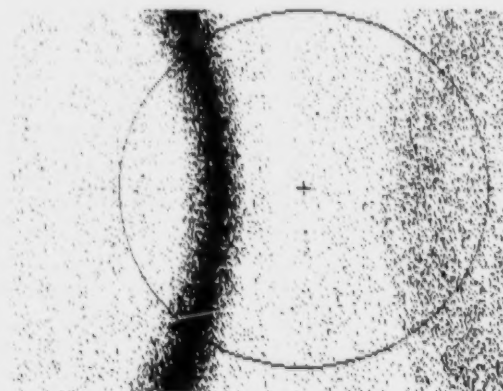


Figure 3. Sensitivity of line array of initial phased array system, projected as shown at left.

Figure 2 demonstrates the geometry for the phased array receiver on the ice. The pattern below the array represents the projection of its sensitivity pattern, when it is steered in a direction as indicated. Here, the darker regions indicate directions of higher sensitivity. This type of projection was used in the design of the array configuration for the current oil detection system. Many different configurations were considered, and their sensitivities were determined using computer modelling. The resulting projections allowed detailed comparison of main lobe width and side lobe strengths and positions, with respect to configuration type, size and steered direction. Figure 3 illustrates the sensitivity of the line array of the earlier system. It can be clearly seen that while resolution in the steered direction is good, there is no discrimination in the perpendicular direction. To achieve such discrimination, a large number of two-dimensional configurations were modelled, and two were finally selected for construction. These are shown in figure 4(a) and (b). The oval was chosen for its precise resolution and by sidelobes, while the cross was also constructed as it would allow multiplicative processing to be tested (of which more later). Figure 5(a) and (b) shows the projected sensitivities of these two arrays.

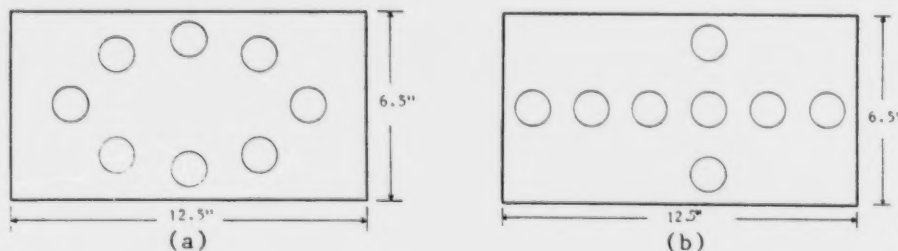


Figure 4. Phased array configurations for present field apparatus: oval (a) and cross (b).

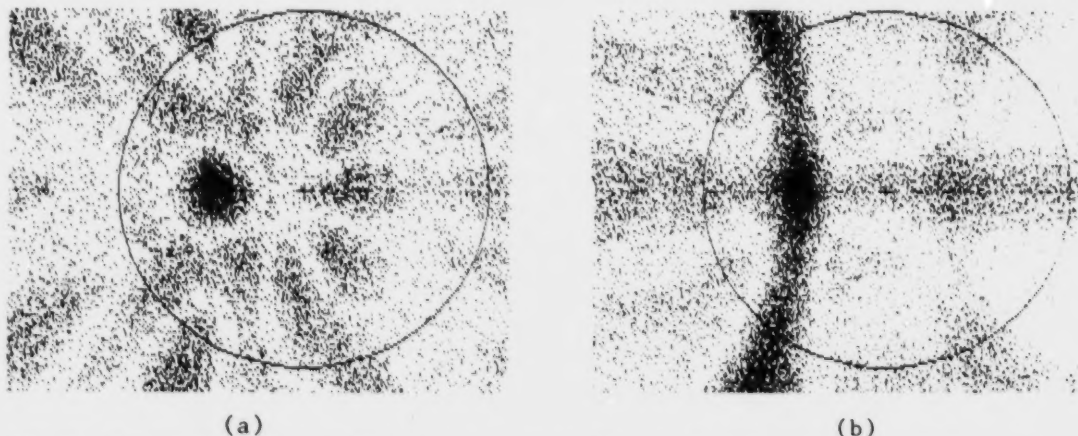


Figure 5. Projected sensitivity patterns for oval (a) and cross (b) array configurations of figure 4.

For both arrays constructed, the main lobe width was measured experimentally using straight path transmission in fresh-water ice. The results are shown in figure 6(a) and (b). The oval has a narrow beamwidth in all directions, which is necessary for thorough noise exclusion. The main lobe of the cross, though wider in the transverse direction, is narrower in the steered direction, which gives better scanning resolution and thus more accurate determination of ice depth.

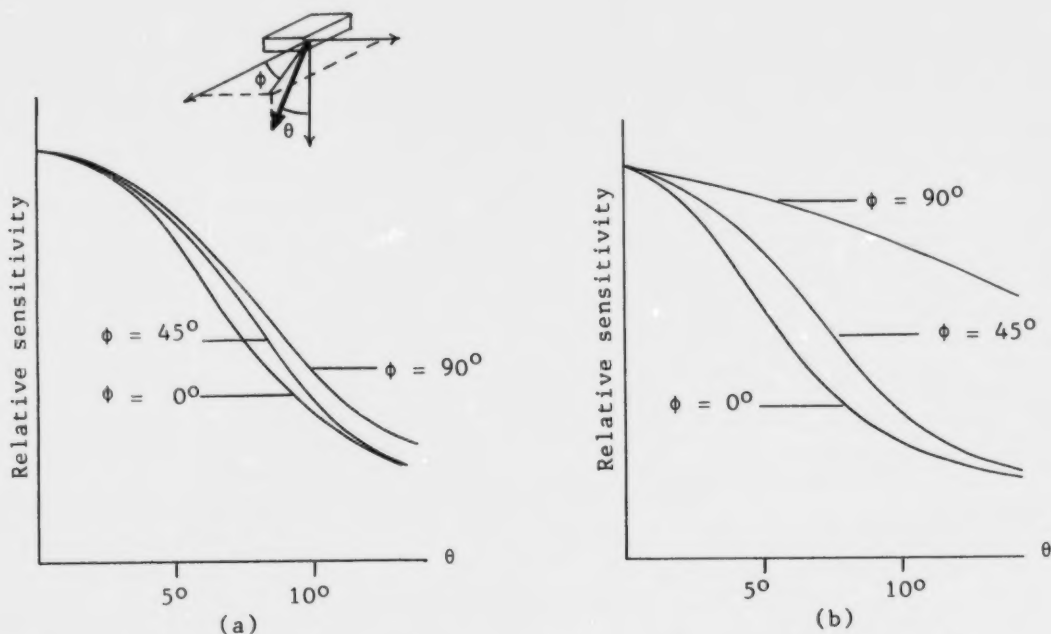


Figure 6. Main lobe widths for oval (a) and cross (b) arrays, from experimental measurements.

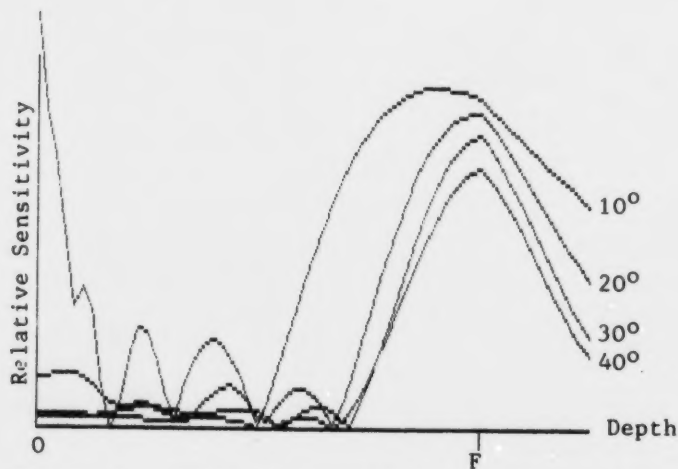


Figure 7. Vertical sensitivity of line array of 8 elements for several values of θ . "F" is the focussed depth.

While the analysis described above is primarily concerned with angular resolution, for some operations vertical resolution is the important consideration, particularly when scanning to locate the bottom interface. At low angles from the vertical, a narrow beam will correspond to a large variation in depth. For this reason operation at angles larger than 15° is considered necessary. Figure 7 illustrates the sensitivity of a line array to reflections from interfaces at various depths, for four angles of incidence. The improvement with increasing angle can be clearly seen.

In general, the sensitivity pattern of an array does not vary with distance from the array. However, there is always a region close to the array where this is not true. This is called the near-field region, its extent being determined primarily by the total size of the array. Within the near-field, diffraction effects dominate, and the sensitivity oscillates rapidly between local minima and maxima. Visualization of a source within this zone is consequently very difficult. For the oil detection system, focussing of the array is employed to greatly reduce near-field difficulties when operation on thin ice is desired. Figure 8(a) and (b) illustrates the sensitivity of the array in a vertical plane directly below it, first for the unfocussed case and then for the array focussed at 20 cm vertical range. The main lobe is split in the unfocussed case and thus the sensitivity is far less than for the focussed array in the steered direction.

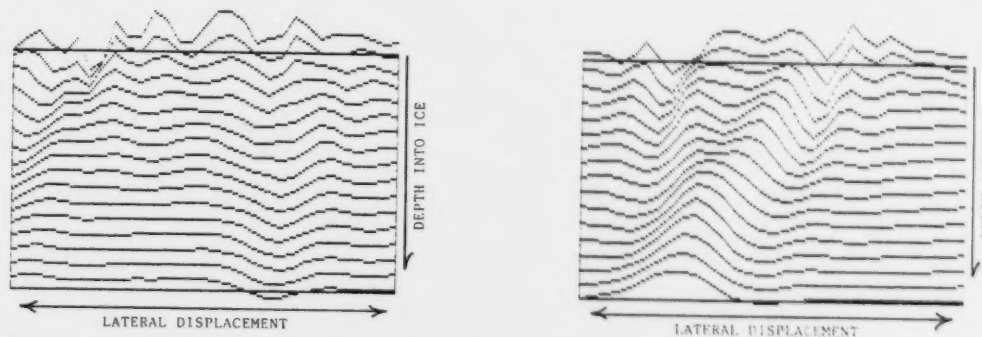


Figure 8. Sensitivity of a line array 28 cm long, in a vertical plane below it of dimensions 24×24 cm, for the unfocussed case (a) and for the case where the array is focussed at 20 cm down (b).

In order to determine the steering directions for the bottom-reflected compressional and shear waves, it is necessary to know the ice depth and wave velocities. Because sound velocity in ice varies quite substantially with temperature, salinity and growth rate, it is not possible to determine ice depth by straightforward time-of-flight measurement. However, we have developed a scanning method which is able to resolve the speed/distance ambiguity. The array main lobe is steered sequentially in increments equal to about half its angular width, over the full steerable range. For each angle the summed signal is time gated so that only that portion of the signal is examined that corresponds to the possible range of velocities for a bottom-reflected wave at the angle in question. The maximum response is then determined, giving both an apparent angle θ_a , and

time of flight T . The ice depth R and compressional velocity c_p are calculated by:

$$\sin^2\theta = \sin\theta_a S / \bar{c}_p T \quad (1)$$

$$R = S / 2\tan\theta \quad (2)$$

$$c_p^2 = S \bar{c}_p / T \sin\theta_a \quad (3)$$

where $\bar{c}_p$ is the mean velocity of the allowed range and S is the receiver-transmitter separation distance.

In addition to the linear processing technique, in which the signals from all elements are summed, there is also the possibility of using multiplicative processing. The most common type of multiplicative array is the Mill's cross⁹, in which the signals along two perpendicular lines of receivers are added separately, and the resulting signals are multiplied together or correlated. Such arrays have particularly high resolution due to an almost complete absence of sidelobes. Figure 9 illustrates the projected sensitivity pattern of the cross array shown in figure 3(b), using multiplicative processing. Software has been developed to analyze data using this technique, and this has been tested on a variety of field data. However, due to the uneven directional distribution of the scattering noise, the enhancement in the pulse recognition was not as great as might be expected. Furthermore, this improvement was offset by a loss in precision of amplitude measurement, which was caused by the spectral distortion that is an inevitable result of non-linear processing.

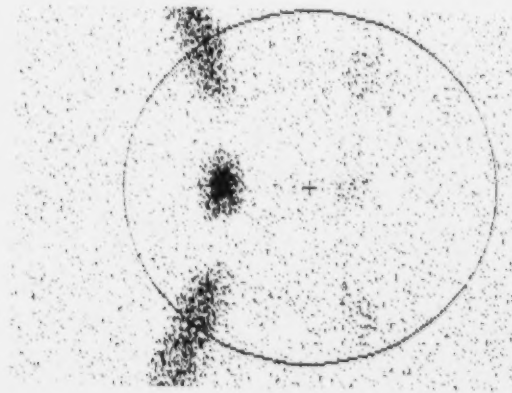


Figure 9. Projected sensitivity of cross array of figure 4(b), using multiplicative processing.

The mechanical construction of the phased array has also been substantially improved from the previous version. Each receiving transducer is now constructed as a separate module which can be readily replaced in the case of failure. As illustrated in figure 10(a) and (b), these modules consist of an aluminium containing cylinder, piezoelectric crystal, aluminium conical matching layer with attachment flange, and backing layer. The backing layer consists of a cylinder of tungsten-loaded epoxy hardened in a centrifuge. This material

loads the receiving element, and prevents internal reflection of the received signal because of its high attenuation. In addition, a small test crystal is mounted at the far end of the backing layer for diagnostic purposes.

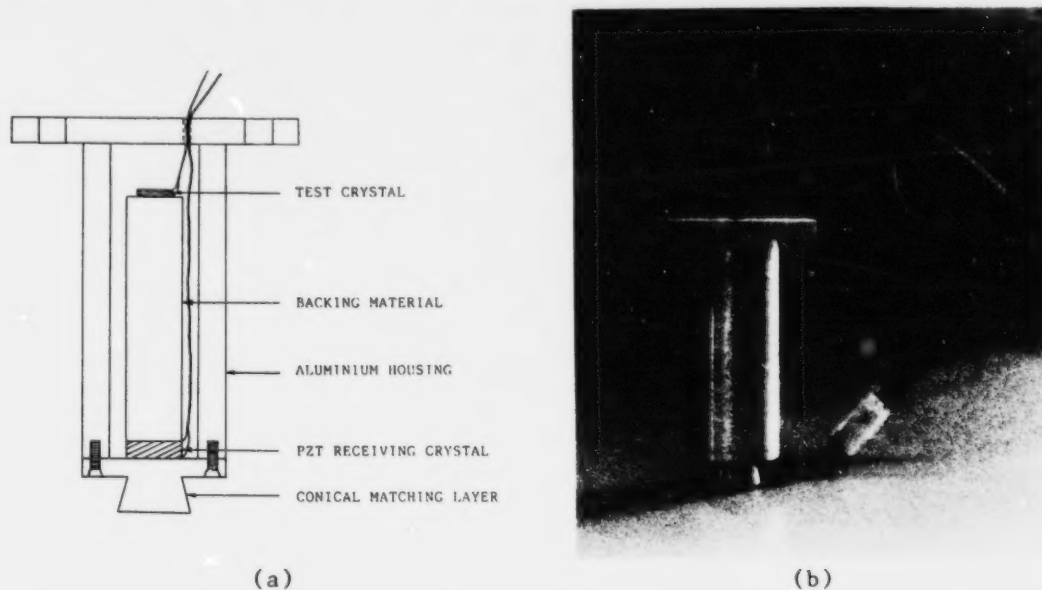


Figure 10. Mechanical construction (a) and finished appearance (b) of individual elements of phased array receiving system.

Earlier arrays employed separate shear crystals for recognition of the shear waves, but these did not function well due to the difficulty of achieving a shear bond with the ice. The present transducers match easily to the ice surface, and in addition to detecting compressional waves they have adequate sensitivity to shear waves by mode conversion at the matching layer. Heating coils on the conical ends are used to melt the individual elements firmly into the ice surface.

PROTOTYPE FIELD INSTRUMENT

The present apparatus operates in the same way as did the earlier laboratory version^{6,7}. However, the main unit has been drastically reduced in size, and is now as shown in figure 11. A specially designed computer interface board has allowed the elimination of the camac crate, and other components such as the transmitter driver and power supplies have been reduced in size and weight. The multiplexers have been moved to the phased array housing, so that only a single signal line, control lines and power lines are now contained within the array cable. The system has operated readily with transducer cable lengths of up to 150 feet. Power is provided either by 12 volt batteries or by portable AC generator. All components are designed to withstand considerable mechanical vibration and impact without failure.



Figure 11. Main unit of present field instrument, with keyboard.

The control software is contained on a ROM drive in the on-board IBM PC computer; the floppy disk drives have been retained for development purposes only and are not needed for field operation. This software is menu driven for ease of operation, and all functions proceed automatically with a minimum of user input. The system is designed for use by a single operator with a minimum of specialized training. A self-testing system is built in which allows the system to automatically trace a failure, and then direct the user in replacement of a faulty unit.

FIELD RESULTS

Tests of the initial phased array apparatus were conducted at the Esso test basin at Esso Resources Ltd., Calgary, Alta. These tests were on salt ice approximately 50 cm thick. Containers of oil were placed under the ice by divers and the oil released at a known time while measurements were being taken. Repeated readings at a variety of angles of incidence of the transmitted pulse were taken, and these clearly demonstrated the presence of oil.

The first field trial of the present apparatus was conducted on the MacKenzie River at Norman Wells, N.W.T., with the co-operation of Esso Resources Ltd. Figure 12 shows the transmitter mounted on the ice and the receiving array tilted to one side to show the individual elements. Here the scanning routine was used to measure the ice thickness initially, and then these measurements were verified by drilling. The scanning results proved accurate to within a few cm in a variety of ice depths from about 80 to 95 cm. Attempts were then made to locate natural oil seepages under the ice. Difficulties were encountered due to the swift under-ice currents and the minute amounts of oil involved. However, one oil site was located in this way, and anomalous oil predictions

were made by the system on only about 10% of readings. Most failures occurred at sites close to the shore, where the ice was severely broken and the bottom surface highly irregular. The ability of the instrument to withstand rough handling and severe environments was certainly demonstrated, as ambient temperatures were generally from -30°C to -40°C . Further field trials are now underway on salt ice on the Beaufort Sea near Tuktoyaktuk. Future minor modifications of the system are envisaged to profit from the increasing experience of a variety of ice and weather conditions.

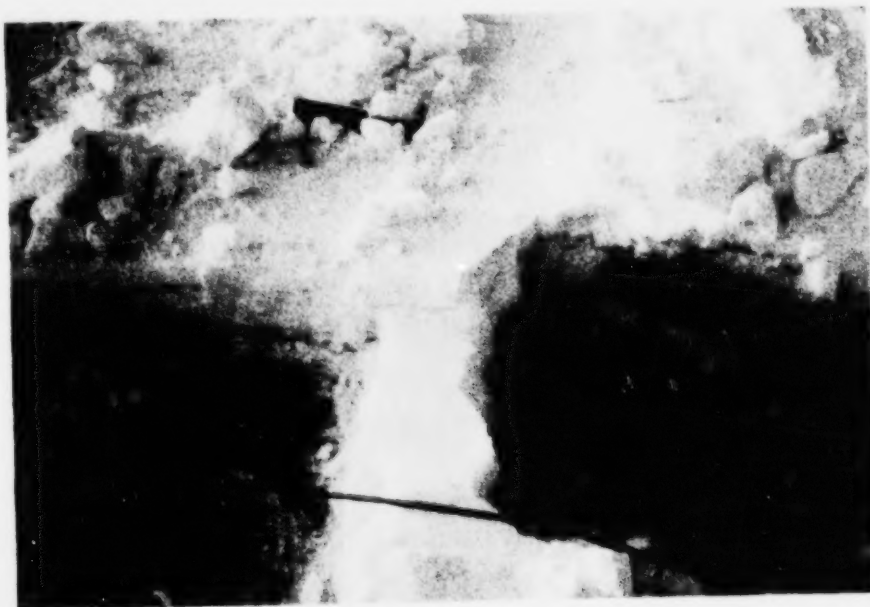


Figure 12. Transmitter and receiving array on ice at Norman Wells.

CONCLUSION

A method has been developed for the acoustic detection of oil trapped under arctic ice. A portable field apparatus has been described. This apparatus has proved to be rugged and reliable; however, further testing is needed to establish its efficacy in a wide variety of arctic conditions.

ACKNOWLEDGEMENTS

This work has been supported by Esso Resources Canada, Ltd. and by the Environmental Protection Service of Environment Canada. Once again we express our gratitude to Dr. R. Goodman and M. Fingas for their assistance and support at all stages of the project. We also gratefully acknowledge the dedicated manufacturing work of J. Isenor and A. Feargrieve.

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THE COMPARATIVE TOXICOLOGY OF OIL SPILL DISPERSANTS TO FISH - IMPLICATIONS
FOR CANADA'S DISPERSANT TOXICITY GUIDELINES AND THE
PROTECTION OF MARINE ENVIRONMENTAL QUALITY

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INTRODUCTION

In 1973, Guidelines on the use and acceptability of oil spill dispersants (Anonymous, 1973) were published in Canada as a first step towards controlling the toxicity and effectiveness of dispersants considered for use in Canadian marine waters. Revised Guidelines were published in 1984 (Anonymous, 1984).

The approach prescribed in the new Guidelines is to determine first whether a selected dispersant achieves a minimal level of effectiveness, using a pass/fail criterion. The effectiveness test is conducted using a standard oil and the dispersant in the Mackay-Nadeau-Steelman apparatus with seawater under standard conditions (Anonymous, 1984; Abbott, 1984). The pass/fail criterion is that 50 percent of the test oil must be dispersed at an application ratio no greater than 1:10 (dispersant:oil).

The dispersant is also subjected to a simple pass/fail test for acute aquatic toxicity. The toxicity test is conducted using fingerling rainbow trout exposed to solutions of dispersant and reference toxicant in freshwater for 96 hours under standard conditions. Existing data on the acute toxicity of dispersants, together with practical considerations (i.e. cultured widely, easily obtained and maintained, acceptable sensitivity), suggested that the rainbow trout was a suitable organism for the test (Sprague, 1969; Doe and Wells, 1978; Wells and Moyse, 1981; Wells, 1982). The fish toxicity test is conducted only at a concentration of 100 mg/L dispersant. The passing criterion is that the median lethal time (LT₅₀) for the organisms exposed to dispersant must exceed 96 hours. In some cases, where the dispersant is very effective but fails the toxicity test, a second toxicity test is conducted at a concentration derived from the effective dispersant:oil ratio.

All products passing the toxicity and effectiveness criteria are placed on an acceptability list for consideration for use in Canadian marine waters.

To date, most marketed dispersants are formulated for use in saltwater. It is well known that salinity influences effectiveness ratings (Wells and Harris, 1979; Lehtinen, 1984; among others), due perhaps to the different solubilities, behavior and complexing actions with hydrocarbons and oil droplets of the dispersant components in seawater (Mackay et al., 1985). Salinity also influences the acute toxicities of selected hydrocarbons and dispersants (Eisler and Kissil, 1975; Wilson, 1977; Levitan and Taylor, 1979; Linden et al., 1979; Neff, 1979).

Hence, there were two concerns with the selected Canadian toxicity protocol - the medium and the test species. While salinity is considered to be a minor modifying factor in toxicity screening tests with most materials (Sprague, 1985), and for dispersants in particular (Wilson, 1977), there is the continued argument that a saltwater test would have been more suitable. Saltwater species are often thought to be more sensitive than freshwater species, due to differences in or lack of osmoregulation, and the greater diversity of species. Hence, most other countries test dispersants in saltwater tests (Wells, 1982; Moldan and Chapman, 1983; Thompson, 1985), their choices being based on practicality, adoption of the British testing protocol (Blackman *et al.*, 1978), or the desire to work with endemic marine organisms.

This study addressed the key question: How important are the factors of species of fish and salinity to the outcome of the single acute toxicity screening test as presently recommended in the 1984 Canadian Guidelines? Experiments were conducted with the rainbow trout, the threespine stickleback and four current dispersants.

We also discuss the choice of testing protocols for dispersants within the wider context of protocols being used in other countries and the role of dispersants to minimize the adverse effects of spilled oils.

EXPERIMENTAL WORK

Methods and Materials

Fingerling rainbow trout, *Salmo gairdneri*, as recommended in the Guidelines, and threespine stickleback, *Gasterosteus aculeatus*, were chosen as the test organisms.

Threespine stickleback were selected due to local availability, ease of collecting, holding and feeding, sensitivity relative to the rainbow trout, sensitivity to oils and dispersants (Wells and Harris, 1979, 1980), and previous recommendations on their suitability (E.V.S., 1977).

The trout were hatchery-reared with a mean weight of 1.27 g (range 0.4-3.6, $n = 1080$). The stickleback were caught by seining wild populations and acclimating them to laboratory conditions. The mean weight was 0.7 g (range 0.2-1.8, $n = 2280$). Acclimation of stickleback to freshwater was achieved by lowering the salinity 3‰ per day and holding in freshwater for one week before testing. Carbon-filtered and ultraviolet-dechlorinated municipal freshwater (Wells and Horne, 1977) was used for holding and for dilution in toxicity tests.

The hardness ranged from 12.1 to 24.4 mg/L for calcium carbonate. Residual chlorines were removed by aerating for 24 hours before commencing a test. Other water properties were described by Wells and Horne (1977).

The saltwater tests were conducted with filtered Bedford Basin seawater taken from a 10 m depth. Salinity ranged between 30.0 and 31.2‰. Preliminary tests were conducted to determine the LC50 ranges for the

stickleback in both freshwater and seawater using four dispersants and the reference toxicant, dodecyl sodium sulfate (DSS). Trout data were examined to choose the final range of dispersant concentrations.

The dispersants used in this study were two concentrates, Corexit 9527 and BP 1100 WD, and two conventional dispersants, Corexit 9550 and DREW LT. Dispersant composition is generally described in Wells (1984) and Canevari (pers. comm.). Storage of dispersants was at 4°C in 250 mL polyethylene containers, and initially in five gallon cans. Corexit 9550 had been stored two years and the other dispersants up to five years. Toxicity test results were compared with those obtained following receipt of dispersants (Doe and Wells, 1978; Wells and Harris, 1980; unpublished data).

All tests were conducted in 40 litres of test solution in cylindrical tanks lined with polyethylene. Each test was aerated at the rate of 200 mL/min to maintain a dissolved oxygen level of greater than 60 percent saturation. All tests were conducted at $15 \pm 1^\circ\text{C}$ with dissolved oxygen (DO) and pH monitored daily. Each dispersant was added on a weight to volume basis, directly to the tank. The reference toxicant DSS was prepared by mixing one gram into one litre of freshwater and stirring until totally dissolved. A control was run for each LC50 determination. Ten fish were used per concentration. Each LC50 determination was performed a minimum of three times and the test duration was 96 hours.

The 96 hour LC50's and 95 percent confidence limits were calculated by the BMD 03S probit analysis program or the graphical method of Litchfield and Wilcoxon (1949), using nominal concentrations of dispersant. The median lethal times (LT50) were calculated graphically (Litchfield, 1949). The LC50's were compared using the equation of Sprague and Fogels (1977).

Results and Discussion

There are several common difficulties in assessing the toxicity of dispersants. There is seldom information about the nature and concentration of the individual components of the formulations. Another difficulty involves the differences in solubilities of dispersant components between fresh and seawater. For example, Corexit 9527 is a concentrate dispersant consisting of three non-ionic and one anionic surfactants within a solvent, ethylene glycols (Wells, 1984; Wells et al., 1985). It is soluble in freshwater and hydrocarbon solvents, and in seawater it is dispersable and not completely soluble (Esso, 1978). Several of the other dispersants (e.g. Corexit 9550 and DREW LT) are also dispersable in water. In this study, results are expressed using nominal concentrations of total dispersants, and do not account for the dissolved, colloidal and possibly sub-particulate phases of the tested mixtures, and differences that may occur between these phases in freshwater and seawater.

Results of the toxicity tests are summarized in Tables 1-3. There were no significant differences between the toxicities derived in this study and those estimated upon initial receipt of the dispersants (Table 2), indicating that the acute toxicities of the dispersants did not change over time. Comparison of results of the three experimental groups for each of

TABLE 1 - COMPARISONS OF 4-DAY LC50'S FOR FOUR DISPERSANTS, TESTED WITH FINGERLING RAINBOW TROUT IN FRESHWATER AND THREESPINE STICKLEBACK IN FRESHWATER AND SEAWATER

Dispersant	Rainbow Trout (fresh)		Threespine Stickleback (fresh)		Threespine Stickleback (salt)	
	LC50*	CL**	LC50	CL	LC50	CL
Corexit 9527	108	R100-320***	46.8	3.4-90	24.3	15-33.7
	170	R100-320		R (100-180)	33.8	25.4-42.2
	134.1	84.5-183.8	103.5	81.8-125.2	39.0	27.1-52.0
Corexit 9550	1030	R750-1800	388	215-561	3200	
	970	R320-1800	1036	343.5-1729	3200	
	1520.1	1150.8-1889.4	776.6	341-1212.3	3200	
BP 1100 WD	120	R56-180	85.2	61-109.3	280.8	208.6-353.1
	157.7	116.5-198.8	69.8	39.6-100	195.3	83.1-307.6
	126.4	69.8-183.0	90.5	62.3-118.8	268.4	195.2-341-6
	150.0	R56-180				
DREW LT	963.6	704.2-1223	520	260.7-779.3	1100	R560-1800
	1090	R560-1800	369.3	240.2-498.1	1170.8	837.8-1503.8
	1020	R560-1800	237	117-352	768	548-988
					976	693-1258
Reference	3.6	3.1-4.2	2.3	1.1-3.5	1.05	R.32-2.7
Toxicant	5.3	R3.7-7.2	2.2	1.2-3.3	.88	.68-1.1
DSS	5.2	R3.7-7.2	3.2	R2.7-5.6	.76	R.56-1.0
	5.6	R3.7-7.2	1.9	R1-2.7		
	4.5	R3.7-5.6				

* 4-day LC50 (median lethal concentration)

** 95% confidence limit

*** R-range of 0% mortality concentration to 100% mortality concentration.

TABLE 2 - COMPARISON OF THE INITIAL 96 HOUR LC50 VALUES WITH FINGERLING RAINBOW TROUT VERSUS THE VALUES ACHIEVED IN THIS STUDY

Dispersant	LC50 Values (Ranges)	
	Initial (1977-1980)	This Study (1985)
Corexit 9527	140-223	108-70
Corexit 9550	1000-1100	970-1520
DREW LT	1000-1100	964-1090
BP 1100 WD	120-180	120-158

TABLE 3 - TOXICITY RANKINGS OF FOUR DISPERSANTS - TESTING WITH FINGERLING RAINBOW TROUT IN FRESHWATER AND THREESPIKE STICKLEBACK IN BOTH FRESH AND SEAWATER

Fingerling Rainbow Trout	Threespine Stickleback	
Freshwater	Freshwater	Seawater
Corexit 9550	Corexit 9550	Corexit 9550
DREW LT	DREW LT	DREW LT
Corexit 9527	Corexit 9527	BP 1100 WD
BP 1100 WD	BP 1100 WD	Corexit 9527

four dispersants and the reference toxicant DSS showed significant but minor differences between experimental groups.

There was no significant difference between LC50's for DREW LT for fingerling rainbow trout in freshwater and threespine stickleback in saltwater. However, stickleback in freshwater were more sensitive than either trout in freshwater or stickleback in saltwater. The results for BP 1100 WD followed a similar pattern. The LC50's for trout in freshwater and stickleback were within a factor of 2 of each other. But again, as with DREW LT, the sticklebacks in freshwater were less tolerant than the other experimental groups. The LC50's for Corexit 9550 were the most variable in comparison to the other dispersants. Corexit 9550 was the least toxic dispersant, based on the nominal LC50's. This was largely due to its immiscibility in water. The dispersant was not uniformly mixed in the water column, making portions of it, particularly the solvent, unavailable to the test organisms. Consequently, the LC50's for Corexit 9550 are high by an unknown amount.

The Corexit 9527 results differed from the other dispersants in that the most toxic responses were from the stickleback in saltwater. This was probably due in part to differences in dispersibility between fresh and saltwater, the dispersant being made for saltwater use only. The LC50 values differed significantly from those of the other two experimental groups. Toxicity tests by Wells and Harris (1980) on the oil spill dispersant, Corexit 9527, and fingerling rainbow trout in freshwater resulted in 4-day LC50's of 140-233 mg/L. A toxicity test from the same study with Corexit 9527 and stickleback in seawater resulted in a 4-day LC50 value of 28 mg/L. These results suggested that stickleback were more sensitive to Corexit 9527 than trout, and agree with those of this study. The increased sensitivity in saltwater may be due also to the greater bioavailability of Corexit 9527 surfactants in higher salinities, due to the improved dispersability of the dispersant and the oral uptake of seawater by the osmoregulating fish.

The toxicity test results for the reference toxicant, DSS, indicated that each group of fish was of relatively equal sensitivity, with stickleback in saltwater being the most sensitive, followed by stickleback in freshwater and trout. The DSS results in this study agreed well with previous results in our laboratory (Pessah *et al.*, 1977; and unpublished data).

The relative ranking of dispersants based on their acute toxicities generally remained the same in each experimental group and the differences between groups, although significant in some cases, remained small (Table 3). Wilson (1977) also found that salinity was of minor importance when he examined the toxicity of nine dispersant products to larvae of haddock, herring, English or lemon sole, pilchard or plaice. Sprague (1985) concluded that "salinity per se does not greatly modify the toxicity of pollutants ... what is important is the genetic nature of the organism (marine, euryhaline or freshwater) and whether it can adapt to a given salinity, hence affecting its tolerance to pollutants". The overall opinion of the toxicology committee for the new Canadian Guidelines concurred with these conclusions (Wells, unpubl. notes).

For the purpose of screening oil spill dispersants to be used in Canadian marine waters, a toxicity protocol with fingerling rainbow trout in freshwater appears to be suitable. However, further studies on the physical/ chemical behaviour of dispersants in fresh and saltwater are required to understand more completely the conditions to which the organisms are exposed. In addition, the limitations of single-species toxicity tests in the regulatory process must be appreciated (Cairns, 1983; Mount, 1986); the best evidence of the environmental safety of dispersants is gained from field or simulated field experiments with initially approved products and oils, as shown in Allen (1984), API (1985), Koons and Vilardi (in prep.), among others.

GENERAL DISCUSSION

The selection of appropriate toxicity testing protocols for dispersants continues to be of concern to countries considering effective oil spill countermeasures. Recent papers by Wilson (1981), Wells (1982), Moldan and Chapman (1983) and Thompson (1985) discuss the objectives and design of such tests, and several countries such as Australia and Brazil are actively working on protocols suitable for their coastlines and specific concerns.

There is an urgent need for more international discussion and consensus on the minimal toxicity test requirements for dispersants. Canada, in its new Guidelines (Anon., 1984), purposely chose a simple screening toxicity test for dispersants alone, linked to and conducted after the effectiveness test, thereby ensuring that the most effective products would be considered for use, and that the complexities of accurately testing oils would be avoided (Wells et al., 1984; Anderson et al., 1974). Many countries seem to favor experimental comparisons of oils versus chemically dispersed oils in their screening process for dispersants, particularly following from the innovative procedure developed in the U.K. (Blackman et al., 1978). Most countries are working with endemic species, or endemic and "standard" species together, under conditions appropriate for their waters. The primary difference in approaches is in the decision to test dispersants alone, dispersants and dispersed oil, or oil and dispersed oil. This difference stems from the choice of different objectives - having a licensing or acceptability test for the new dispersants alone, or having reliable, acute and chronic toxicity tests that allow some prediction of the comparative field effects of dispersed versus undispersed oils.

Countries must consider their objectives carefully, particularly considering the limitations of acute, single species tests (Cairns, many pubs.), the need for some international uniformity of testing protocols for dispersants, and the very real technical and practical constraints around regulatory tests with oils. Canada has chosen a two-stage screening test to eliminate products of low effectiveness and unacceptably high toxicity. Environment Canada is reviewing the choice of test species as shown in this paper, and has supported evaluations of the comparative ecological effects of oils alone and chemically dispersed in shallow north temperate and arctic marine waters.

We encourage continued discussion of the relative merits of the different approaches for appraising dispersants, in the interests of efficiently approving products to reduce the known acute and chronic impacts of oil spills (NRC/NAS, 1985), and protecting marine environmental quality. The current NRC review of the effectiveness of dispersants (NRC Marine Board, Wash., D.C.) is a positive step towards this goal.

CONCLUSIONS

(1) The choice of the fingerling rainbow trout as the toxicity test organism in Canada's dispersant guidelines is supported by the above experimental study.

(2) However, the choice of an acute, single species, screening toxicity test may bias the comparisons of relative toxicities of products or their component chemicals, and may limit the overall evaluation of their environmental safety. Hence, we encourage more extensive marine ecotoxicological studies with dispersants on any country's acceptability list, particularly addressing the comparative fate and effects of dispersed and undispersed oils in sensitive shore and nearshore environments.

(3) There is a continued need for formal international discussion of the basic elements of dispersant testing procedures in order to (a) simplify and standardize dispersant licensing tests, (b) allow reliable comparisons of data from one country to another, and (c) ensure that the known principles of dispersant and hydrocarbon toxicology are applied to evaluations of the impacts of chemically dispersed oils in polar, temperate and tropical coastal waters.

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Organism Exposure to Volatile Hydrocarbons From
Untreated and Chemically Dispersed Crude Oils
in Field and Laboratory

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INTRODUCTION

This paper reviews American Petroleum Institute sponsored projects that measured the volatile/soluble hydrocarbons (C_1 to C_{10}) in field and laboratory studies and compares field exposure with those in the laboratory, along with other published laboratory studies that have measured dissolved hydrocarbons in exposure waters.

When oil is spilled on a quiet water surface, only soluble components in the oil can affect organisms in the underlying water. Contributed hydrocarbons are principally those with less than 10 carbon atoms in the molecule. The aromatic hydrocarbons naphthalene and mono- and dimethylnaphthalenes (C_{10} to C_{12}) contribute lesser amounts (Anderson et al., 1974; McAuliffe, 1979; Rice et al., 1977). Concentrations of saturate (alkane and cycloalkane) hydrocarbons in water in equilibrium with crude oils are about equal to the sum of aromatic hydrocarbons. Benzene and toluene comprise from 70 to 85% of the dissolved aromatic fraction in water equilibrated with Murban, La Rosa, South Louisiana, Kuwait, Cook Inlet, and Prudhoe Bay crude oils (McAuliffe, 1979).

Most waters, however, are not quiet and waves and currents mix (at least momentarily) separate phase oil into the underlying water. Depending upon the oil and the mixing energy, natural breakup of the slick occurs with droplets of oil remaining in the water column. This breakup of the slick can initially increase the rate of solution of hydrocarbons in surface water, but the competing process of evaporation to the atmosphere appears to dominate (Harrison et al., 1975).

Natural dispersion of oil slicks can be greatly accelerated by spraying it with a chemical dispersant that lowers oil-water interfacial tension. Dispersed oil concentrations in water greatly exceed those that occur naturally. However, the soluble/volatile hydrocarbons appear to be quickly lost to the atmosphere more quickly than from the undispersed surface slick (McAuliffe, 1980).

There have been a large number of laboratory bioassays conducted with the water-soluble fraction (WSF) obtained by equilibrating an excess of crude or refined oils with water. This fraction has been selected, and rightly so, because it is generally believed that the dissolved hydrocarbons cause immediate toxic effects on marine and fresh water organisms. The WSF has also been used because it has simplified bioassay testing that is difficult with oil that adheres, for example, to vessel walls and organisms.

The results of some of the API studies are presented in greater detail because the information is in reports in press or in final draft form, but not yet generally available. Published studies are summarized in lesser detail. Field and laboratory organism exposures are compared to place observed biological effects in perspective. Only investigations that have measured dissolved hydrocarbons in exposure waters have been included. A comprehensive literature survey has not been attempted.

API SPONSORED BIOASSAYS AND BEHAVIORAL STUDIES

Several studies have been conducted with adult and fry salmon at the University of Washington, Fisheries Research Center, Seattle, and on herring at Battelle Pacific Northwest Research Laboratory, Sequim, Washington. In these and other studies reported here, organism exposure has been reported as concentration times time and expressed as ppm-h (Anderson et al., 1984). The LC₅₀ value can be calculated by dividing ppm-h by the length of exposure. All values are in mg/L total C₁ to C₁₀ hydrocarbons, or as total aromatic hydrocarbons (C₆ to C₁₀ plus naphthalenes), or for individual hydrocarbons.

University of Washington

University of Washington researchers (Brannon et al., 1985; Nakatani et al., 1983, 1985; Nevissi and McAuliffe, 1986) measured the effects of untreated and chemically dispersed Prudhoe Bay crude oil on the homing of (a) adult chinook salmon in freshwater, and (b) adult coho salmon in seawater; and the amounts of these oils to cause half-kill (LC₅₀) of (a) adult coho salmon, and (b) chum salmon fry.

Chinook Salmon Homing

The selected oil concentrations for salmon exposure were 0.5 mm thick oil, and 105 ppm dispersed oil, greater than expected during an oil spill as discussed later.

Three days each week between October 9 and November 6, 1981, 24 adult chinook salmon (*O. tshawytscha*) averaging 62 cm fork length and 2.7 kg were seined from the university hatchery pond, anesthetized, tagged, and used in homing and longevity experiments (Nakatani et al., 1983). After 1 h recovery, six fish were placed in each of four 1.5 m circular tanks holding 1300 L of aerated and circulated lakewater. One tank was the untreated control, a second contained untreated Prudhoe Bay crude oil, the third contained 105 ppm of chemically dispersed crude oil (10:1 oil to dispersant), and the fourth 10.5 ppm of the freshwater chemical dispersant. These tanks were used for all adult salmon exposures including the homing of coho salmon at Big Beef Creek reported later.

After 1 h exposure, the salmon were removed from the exposure tanks, held overnight in a raceway, trucked 9 km downstream, and released. Reentry to the university pond was recorded to the nearest day by monitoring for color-coded tags.

Of the 215 chinook salmon released for remigration, 154 (72%) returned to the university pond (Table 1). There was no significant difference in the percent return, nor in the time it took the fish to return, for control, oil, dispersed oil, and dispersant treated groups.

Table 1. Percent Return and Speed of Second Homing by Chinook Salmon After Four Different Treatments.

Treatment	Number Released	Number Returned	Percent Returned	Days to Return, Mean $\pm$ SD
Control	53	35	66	4.0 $\pm$ 2.9
Oil	54	41	76	2.7 $\pm$ 2.1
Dispersed oil	54	39	72	2.8 $\pm$ 2.1
Dispersant	54	39	72	3.5 $\pm$ 3.0
TOTAL	215	154	72	3.2 $\pm$ 2.6

Because olfaction is essential to homing (Hasler and Scholz, 1983), it was concluded that the olfactory systems were not impaired or at least not sufficiently so to interfere with homing. Histopathological analysis of the olfactory organs (nares) sampled from 72 adult chinook salmon showed no anomalies. Thus, while adult salmon might avoid oil (Weber et al., 1981), forced brief exposure to whole Prudhoe Bay crude oil or chemically dispersed oil at unrealistically high concentrations did not prevent or delay homing.

Oil avoidance was also observed in these studies. Before the untreated oil was added to the exposure tank, the salmon swam throughout the tank. After oil addition, the fish went to the tank bottom and remained there during the 1 h exposure. Rice (1973) mixed Cook Inlet crude oil with water, allowed the oil to separate, and then flowed the water into aquaria to determine pink salmon fry avoidance. The fry avoided water equilibrated with 500 mg of oil/L (a concentration that was lethal after 24 h exposure), but did not avoid a sublethal concentration prepared with 90 mg of oil/L of water.

The total C_1 to C_{10} hydrocarbons in the exposure waters for the untreated and chemically dispersed oil treatments are shown in Figure 1. Oil on the surface slowly introduced dissolved hydrocarbons, with concentrations continuing to increase at the end of 1 h. However, total C_1 to C_{10} hydrocarbons in the dispersed oil tank attained their highest concentrations in 10 to 15 min, then decreased.

Coho Salmon Homing

The studies were conducted with adult coho salmon (*O. kisutch*) in marine waters of Hood Canal at the University of Washington, School of Fisheries, field station at Big Beef Creek. The study methods were the same (tanks,

exposure time, oil concentrations, etc.) except that coho salmon were used instead of chinook, sea water was used in holding and exposure tanks, and the tanks were in the open instead of in a building.

The treated fish were released at King Spit 7 km from Big Beef Creek (Nakatani et al., 1985). Table 2 presents the percent return and speed of the second homing after four different treatments.

Table 2. Percent Return and Speed of Second Homing by Coho Salmon After Four Different Treatments.

<u>Treatment</u>	<u>Number Released</u>	<u>Number Returned</u>	<u>Percent Returned</u>	<u>Days to Return, Mean $\pm$ SD</u>
Control	81	14	17.3	16.0 $\pm$ 13
Oil	80	20	25.0	15.0 $\pm$ 13
Dispersed Oil	80	14	17.5	16.8 $\pm$ 13
Dispersant	73	14	19.2	15.6 $\pm$ 10
TOTAL	314	62	19.7	15.8 $\pm$ 12

Statistical analysis showed there was no significant difference in percent returns or time to return between the four treatments. Nakatani et al. (1985) concluded that, as for fresh water, there was no reason to believe short-term exposure to Prudhoe Bay crude oil had any deleterious effect on homing success. The mean percent return was very much lower than for the chinook salmon returning to the university pond. This reduction was attributed to the extensive gill net fishery in Hood Canal (Nakatani et al., 1985). There was little fishing pressure on the chinook salmon in freshwater between the release point at Ballard Locks and the university pond.

Bioassays of Adult Coho Salmon

The oil and dispersed oil concentrations used in the homing experiments did not affect percentage return nor the time to return compared with controls in either fresh or seawater. It is desirable to not only relate these exposures to those found in field experiments, but also to determine the concentrations required to kill adult and juvenile salmon.

During the homing experiments at the Fisheries Research Center, some available adult coho salmon were exposed to four different concentrations of oil and dispersed oil for 4 h to estimate an LC₅₀ (concentrations required to cause half kill).

Anderson et al. (1984) showed that linear dilution of dispersed oil to zero concentration in 26 h resulted in toxicity indices or exposures (concentra-

tions x time) quite similar to those for exposures at constant concentrations. For example, an exposure at 10 ppm for 2 h ($10 \times 2 = 20$) would be predicted to have the same biological effect as an exposure at 1 ppm for 20 h ($1 \times 20 = 20$). There are obvious limits to this concept. If the concentration is low and the time long, the organism can metabolize the hydrocarbons with no apparent adverse effect. A very short exposure to a high concentration may not cause mortality during exposure, but the organism dies later. This exposure (dose) relationship probably holds over time intervals from an hour to a day or two as used in this paper. This product of concentration x time is designated as ppm-h (organism exposure).

Table 3 summarizes the bioassay results for the relatively small number of coho salmon exposed to varying concentrations of oil for 4 h. These results show that the LC_{50} for adult coho salmon was >5.0 ppm-h of total C_1 to C_{10} hydrocarbons in the exposure water under untreated oil slicks.

Table 3: Four Hour Adult Coho Salmon Bioassays With Untreated and Chemically Dispersed Fresh Prudhoe Bay Crude Oil

Treatment, Oil or Dispersed Oil Added	Exposure, Concentration of Total C_1 to C_{10} Hydrocarbons x Time (ppm-h)	Fish Mortalities	Post-exposure Mortalities, Days
Control	-	0 of 9	13, 13, 13
Dispersant	-	0 of 12	12, 16
<u>Oil, mm thick</u>			
1.0	2.0	0 of 3	14, 16 *
1.6	2.5	0 of 3	13 *
2.1	5.0	0 of 3	5, 9 *
2.6	3.7	0 of 3	*
<u>Dispersed oil, ppm</u>			
210	10.1	1 of 3	1, 14 *
210	11.6	1 of 3	*
260	14.0	3 of 3	
260	12.8	3 of 3	

* Remaining fish were taken at end of 4 h exposure for histopathology.

These data indicate that longer exposures and/or thicker crude oil slicks would be required to cause adult coho salmon mortality. Table 3 shows the LC_{50} for chemically dispersed oil to lie between 210 and 260 ppm. Total C_1 to C_{10} hydrocarbons measurements indicate that half-kill is approximately 12 ppm-h.

Chum Salmon Fry Bioassays

Toxic bioassays were conducted with chum salmon fry in sea water at 10°C in 20 litre pyrex glass water baths. The fish were 5 to 8 cm in length, weighed about 0.7 g and 10 fish were exposed in each tank. The testing procedures were the same as for the adult salmon except that there was no pump to circulate the water, and the exposure was for 24 h. Aeration was vigorous to cause water circulation to mix soluble components in the surface slick throughout the water column (Nevissi and McAuliffe, 1986).

Figures 2 and 3 show the total C₁ to C₁₀ hydrocarbon concentrations in water during the 24 h exposure. The C₁ to C₁₀ hydrocarbons increased to their highest concentration after 1 to 3 h under the untreated oil slicks, thereafter decreasing. The C₁ to C₁₀ hydrocarbons from dispersed oil quickly attained their highest concentrations (Figure 3; probably within 10 min as shown in Figure 1), and then were more quickly removed from solution by aeration and surface evaporation than for untreated oil. The exposures as ppm-h were obtained by integrating the area under the curves.

Table 4 relates the total C₁ to C₁₀ hydrocarbons (as ppm-h) to observed fish mortalities that occurred during exposure. There were no post-exposure mortalities of exposed fish during the week that they were held in clean running seawater. The total C₁ to C₁₀ hydrocarbon exposures to cause half-kill are 19 ppm-h for the untreated oil and 9 ppm-h for the chum salmon fry exposed to chemically dispersed oil. These results show that chum salmon fry had about the same sensitivity to untreated or chemically dispersed fresh Prudhoe Bay crude oil as did adult coho salmon.

Table 4: Chum Salmon Fry Bioassays, 24-Hour Exposure.

<u>Treatment, Oil or Dispersed Oil Added</u>	<u>Exposure, Concentration of Total C₁ to C₁₀ Hydrocarbons x Time (ppm-h)</u>	<u>Fish Mortalities During 24-Hour Exposures</u>	<u>Post-Exposure Mortalities, One Week</u>
<u>Oil, mm Thick</u>			
Control	-	0 of 10	None
1.7	9.0	0 of 10	
2.4	11.0	0 of 10	
3.7	14.5	1 of 10	
4.5	22.0	8 of 10	
<u>Dispersed Oil, ppm</u>			
Control	-	0 of 10	None
144	4.4	0 of 10	
288	10.0	6 of 10	
430	18.0	10 of 10	
570	33.0	10 of 10	

Battelle Pacific Northwest Laboratories

Pearson et al. (1985) studied the effect of Prudhoe Bay crude oil and chemically dispersed oil on Pacific herring egg fertilization, hatching, and larval abnormalities in 1982 and 1983. Five exposure levels in flowing systems were used. Table 5 presents the total C₁ to C₁₀ hydrocarbon exposures measured in 1983. The 1982 exposures were similar, but not measured.

Table 5: Total C₁ to C₁₀ Hydrocarbons in the 1983 Exposure Waters of Herring Egg Studies Expressed as ppm-h (concentration x time)

Exposure Level	Control	24 h PBC Oil Exposure ^a		2 h PBC Oil Exposure ^a	
		WSF Filtered	WSF Unfiltered	WSF Filtered	WSF Unfiltered
Control	<0.1				
1 Low		0.93	0.61	0.08	0.05
2		1.4	9.4	0.11	0.78
3 Intermediate		23	30	1.9	2.5
4		108	55	9	4.6
5 High		227	129	19	11

^aC₁ to C₁₀ concentration in mg/L = ppm-h ÷ time

The herring eggs from ripe females were extruded on microscope slides in two rows with about 80 eggs (55 to 148 range) per slide. The slides were replicated. The eggs were then placed immediately in sperm water for 30 min and then in clean flowing sea water until all slides for the various treatments had been fertilized. All slides were then transferred to the exposure waters within a period of 40 min and within 5 h after fertilization. The exceptions were eggs placed in exposure waters before fertilization, and during fertilization.

1982 Egg Exposure to Oil Before Fertilization - Eggs were exposed for 2 h to the WSF of fresh PBC oil, chemically dispersed PBC oil, and to the chemical dispersant at five increasing concentration levels before the eggs were placed in sperm water. There were no differences in percent fertilization of the oil, dispersed oil, and dispersant treated eggs compared with control eggs.

1982 Egg Exposure to Oil During Fertilization - The herring eggs and sperm were added to the exposure waters and held for 2 h. There were no differences in percent of eggs that were fertilized after treatments compared to the controls. Thus, there was no effect on the fertilization process.

Hatching Time - 1982 and 1983 - In both years the herring eggs hatched in the expected number of days and based upon water temperature and salinity, independent of treatment. The hatching times were 12 to 13 days.

Percent Hatch - 1982 and 1983 - In both years there was no effect on percent hatch in any oil treatment (untreated PBC oil, chemically dispersed PBC oil, or dispersant) compared with controls. The 77% hatch for all treatments in 1982 was slightly higher than the 67% in 1983.

Larval Abnormalities - 1982 and 1983 - Three abnormalities were visible under the dissecting microscope: (1) curvature of the spine, (b) swollen pericardial regions, and (c) compartmentalization of the yolk sac.

Abnormalities occurred naturally in control larvae and differed significantly between years, 35% in 1982 and 10% in 1983 (Table 6). In both years, the most severe treatments were the unfiltered oil WSF preparations that had some oil droplets mechanically mixed into the water during the preparation of the WSF. These droplets were sticky and adhered to the eggs as the WSF flowed through the exposure chambers.

TABLE 6: Herring Larvae that Showed Gross Visible Abnormalities After 24-Hour Exposure of Eggs to Untreated Prudhoe Bay Crude Oil, Dispersed Oil, and Chemical Dispersant

Exposure	Percent Abnormal Larvae						
	1982 Treatment				1983 Treatment		
	Control	WSF Unfiltered	Dispersed Oil	Dispersant	Control	WSF Filtered	WSF Unfiltered
Control	35	-	-	-	10.4	-	-
1 Low		52 ^a	46	8		13	19
2		70	36	30		13	19
3 Intermediate		60	34	75		9	36
4		67	87	93		9	25
5 High		81	83	83		13	58
Overall		68	63	63		11.4	31

^aBoxed numbers are significantly different from control abnormalities. See Pearson et al., (1985) for detailed analyses.

Table 6 shows that filtering the PBC oil WSF preparation in 1983 to remove the majority of the mechanically dispersed oil droplets produced no increase in abnormalities compared with the control (10.4 vs 11.4%), although both filtered and unfiltered WSF preparations contained high concentrations of dissolved

hydrocarbons (Table 5). The filtered WSF preparations contained higher dissolved hydrocarbons than the unfiltered, probably due to better contact as the water passed through the collected oil droplets on the filter.

Many times more total oil as droplets of chemically dispersed oil were flowed through the exposure chambers, but the droplets did not adhere to the eggs. At the higher dispersed oil exposures, an oil film was observed on the glass slides and attached eggs.

Table 6 indicates that the dispersant alone (in concentrations equivalent to a 1:20 ratio to that of oil) caused increased larvae abnormalities at the three higher exposure levels. Thus, the increased larvae abnormalities from dispersed oil may be from the dispersant.

The amount of oil adhering to the eggs as droplets appears to have been the major factor determining the frequency of abnormal larvae. Oil on eggs could have been acting both as a more direct route for entry into eggs of toxic components, and as a coating producing oxygen deprivation in the developing embryos. Direct entry is probably the most likely explanation, because oxygen and carbon dioxide both dissolve in crude oils, and a thin film is not likely to appreciably inhibit gas exchange.

These results suggest that chemically dispersing fresh crude oil slicks would produce fewer abnormal herring larvae compared with untreated oil that concentrated on a shoreline and attached to intertidal and perhaps subtidal eggs if the oil mixed downward with wave action.

ADDITIONAL BIOASSAY AND BEHAVIORAL STUDIES

A number of bioassay and behavioral investigations have been conducted where the hydrocarbons in the WSF of crude oils or individual hydrocarbons have been measured in the exposure waters.

National Marine Fisheries Laboratory, Auke Bay

Extensive studies have been conducted with the WSF of Cook Inlet crude oil on 39 marine species (Rice et al., 1979). Test animals were collected in southeast Alaska and were adults or juveniles if the adults were large (e.g., king crab, pink salmon, flounders). Prior to testing, all animals were acclimated and fed in flowing seawater at 4° to 8°C and salinities of 26 to 30‰ depending upon the season. They were not fed during the static 4-day bioassays.

The WSF's of Cook Inlet crude oil were prepared by mixing one percent oil in seawater for twenty hours and allowing it to stand for three hours before use. Water samples for gas chromatography (GC) analyses were extracted by methylene chloride, and a small aliquot of each extract was analyzed by GC for monoaromatic hydrocarbons. Diaromatic hydrocarbons (naphthalenes) required increased sensitivity. Thus, the remainder (most) of the extract was concentrated by evaporation with nitrogen after addition of nC_{10} and C_{16} as internal standards. The saturate hydrocarbons (alkanes and cycloalkanes) although present in the

WSF exposure waters were not measured. The dissolved saturate hydrocarbons comprise from 30 to 50% of the total dissolved hydrocarbons. Thus the exposures in Table 7 and for these studies reported in Table 11 would be correspondingly higher to compared with the total C_1 to C_{10} hydrocarbons reported for the ocean research studies.

The dissolved hydrocarbons in the test waters declined in 96 h, by evaporation and biodegradation, to about 20% of the initial concentration. Exposure solutions were aerated slowly at one bubble per second.

Table 7 summarizes the large number of bioassays that represent pelagic, intertidal, subtidal, planktonic, and benthic marine species. The 96 h LC_{50} values for total aromatic hydrocarbons (as mg/L) have been expressed as "exposure" (ppm-h) of total aromatic hydrocarbons. The 96 h LC_{50} value has been corrected for hydrocarbon loss. For example 96 h LC_{50} of 1.22×0.35 (average exposure concentration for total aromatic hydrocarbons for 4 days) $\times 96 = 41$ ppm-h. A next to last column shows an estimated 24 h exposure using 75% of the initial total aromatic LC_{50} concentration, and assuming the same mortality after 24 h as after 96 h. This is conservative. Making this assumption places the exposure as ppm-h for Dolly Varden and pink salmon closer to those measured for adult coho and chum salmon fry at the University of Washington (Nakatani et al., 1985; Nevissi and McAuliffe, 1986).

Rice et al. (1979) made three arbitrary classifications of sensitivity to total aromatic hydrocarbons. Highly sensitive species, which included most of the pelagic fish and shrimp, had total aromatic hydrocarbon exposures to cause 50% mortality of 20 to 50 ppm-h. The moderately sensitive species had exposures from 50 to 150 ppm-h and included one shrimp, one bottom fish, two crabs, a scallop, and one lower intertidal limpet.

Tolerant species exceeded 150 ppm-h exposure to total aromatic hydrocarbons and did not die in 4 days in the highest concentrations of dissolved aromatic hydrocarbons that could be generated (8-12 mg/L) in seawater from Cook Inlet crude oil. Tolerant species included one bottom fish (starry flounder), two intertidal fish, and most of the intertidal echinoderms, hermit crabs, limpets, chitons, clams, snails, and worms. The most sensitive species were generally pelagic; the moderately sensitive species were either benthic or intertidal forms; and the tolerant species were predominately from the intertidal zone. There were some exceptions, such as the tolerant subtidal amphipods and mysids.

Moles and Rice (1983) measured longterm (40 day) sublethal effects of the WSF of Cook Inlet crude oil and naphthalene using juvenile pink salmon in seawater. The exposures were flow-through (constant concentration) with naphthalene concentrations of 0.12, 0.38, 0.56, and 0.80 mg/L (ppm); and total aromatic concentrations (WSF) of 0.21, 0.40, 0.58, and 0.87. The 96-hour and 40-day LC_{50} for both the WSF crude oil aromatics and naphthalene were 1.20 mg/L. Thus, the long exposure concentrations were from 10 to 73% that required to kill half of the salmon.

Fish responded quickly to the toxicants, and most deaths occurred during the first 12 hours. No fish died after 96 hours.

TABLE 7: Sensitivities of 39 Alaskan marine species to Cook Inlet crude oil - 96 h TLM's are in mg/L (ppm) of total aromatics determined by gas chromatography, with 95% confidence intervals in parentheses (adapted from Rice et al., 1979).

Common Names	Habitat	Total Aromatics	Exposure in ppm-h	
			24 hours ^a	96 hours ^b
<u>Fish</u>				
1. Pacific herring	pelagic	1.22 (0.88-1.56)	22	41
2. Dolly Varden	pelagic	1.55 (1.30-1.80)	28	52
3. pink salmon	pelagic	1.69 (1.47-1.83)	30	57
4. Walleye pollock	pelagic	1.73 (1.37-2.09)	31	58
5. tube snouts	pelagic	2.55 (2.06-3.03)	46	86
6. great sculpin	benthic	3.96 (3.52-4.40)	71	133
7. starry flounder	benthic	>5.34	>96	>179
8. crescent gunner	intertidal	>11.72	>211	>394
9. cockscomb prickleback	intertidal	>11.72	>211	>394
<u>Crustaceans</u>				
10. grass shrimp	subtidal	0.87 (0.83-0.91)	16	29
11. humpy shrimp	subtidal	1.79 (1.53-2.04)	32	60
12. kelp shrimp	subtidal	1.86 (1.66-2.07)	33	62
13. pink shrimp	subtidal	4.94 (3.20-5.60)	89	166
14. king crab	benthic	3.69 (2.65-4.73)	66	124
15. purple shore crab	intertidal	8.45 (8.32-8.58)	152	284
16. hairy hermit crab	intertidal	>10.58	>190	>355
17. amphipod	planktonic	>7.98	>144	>268
18. mysid	planktonic	>9.02	>162	>303
<u>Echinoderms</u>				
19. tarspot	intertidal	>6.84	>123	>230
20. green sea urchin	intertidal	>10.58	>190	>355
21. six-armed starfish	intertidal	>10.58	>190	>355
22. white cucumber	intertidal	>12.29	>221	>413
<u>Mollusks</u>				
23. pink scallop	benthic	3.94 (3.52-4.39)	71	132
24. blue mussel	intertidal	>8.97	>161	>299
25. little neck clam	intertidal	>6.84	>123	>230
26. plate limpet	intertidal	8.18 (6.14-10.96)	147	275
27. shield limpet	intertidal	>8.46	>152	>284
28. leather chiton	intertidal	>8.46	>152	>284
29. lined chiton	intertidal	>8.46	>152	>284
30. ciliated chiton	intertidal	>8.46	>152	>284
31. purple margarite	intertidal	>8.46	>152	>284
32. Sitka periwinkle	intertidal	>8.46	>152	>284
33. file periwinkle	intertidal	>8.46	>152	>284
34. Hall's colus	benthic	>8.46	>162	>284
35. ridged whelk	benthic	>10.58	>162	>355
<u>Annelids</u>				
36. mussel worm	intertidal	>10.58	>190	>355
37. scale worm	intertidal	>10.58	>190	>355
<u>Nemerteans</u>				
38. purple ribbon worm	intertidal	>10.58	>190	>355
39. brown ribbon worm	intertidal	>10.58	>190	>355

^a ppm-h = 24 h LC₅₀ total aromatics x 0.75 x 24
^b ppm-h = 96 h LC₅₀ total aromatic x 0.35 x 96

Control fish and fish exposed to the lowest concentrations of naphthalene (0.12 mg/L) and the water-soluble fraction of crude oil (0.21 mg/L) fed normally throughout the study. When food was introduced, these fish fed vigorously at the water surface and consumed all particles. Exposure to higher concentrations of toxicants affected feeding behavior: for example, fish exposed to 0.38 and 0.56 mg/L naphthalene and 0.40 and 0.58 mg/L WSF of crude oil fed less aggressively and consumed only 80% of the food. Fish exposed to the highest concentration of crude oil WSF and naphthalene lost equilibrium and ate very little food for the first few days of the study; however, during the last week of exposure, these fish ate about 10% of the food offered.

Change in length of the fish was not a sensitive measure of the toxicity of either naphthalene or the water-soluble fraction of crude oil. Only fish exposed for 30 or 40 days to the highest concentrations of each toxicant had shorter lengths than controls.

Fish exposed for 40 days to concentrations of 0.38 mg/L naphthalene and 0.10 mg/L WSF of crude oil (both one-third of the 96 h LC₅₀) weighed significantly less than control fish.

There was little or no effect of hydrocarbon exposures on the caloric content or the fat content of the fish. The exposure concentrations expressed as ppm-h using 24 h exposure were: naphthalene 2.9, 9, 13, and 19; Cook Inlet crude oil total aromatics in the WSF 5, 10, 14, and 21. The first measurement of growth, caloric and fat content were made at 10 days. The exposure in ppm-h were 10 times those shown for 1 day. If the concentrations were made 10 times higher during the first day, fish mortality would have occurred. These long term exposures reveal that fish can adapt to lower concentrations for longer times - probably by metabolizing the hydrocarbons.

National Marine Fisheries Tests of Ballast Water at Port Valdez

Rice et al. (1981) determined the 96 h LC₅₀ for the larvae of five marine species to total aromatic hydrocarbons in the ballast-water treatment effluent of Port Valdez, Alaska. The relative proportions of the dissolved aromatic hydrocarbons in the effluent discharge were very similar to those measured for water equilibrated with Cook Inlet and Prudhoe Bay crude oils. As for the Anke Bay studies, saturate hydrocarbons present in the WSF were not measured. Thus, the values in Table 11 (discussed later) should be increased to compare with the total C₁ to C₁₀ hydrocarbons reported for the field research spills.

The exposure solutions were renewed daily. The water temperatures were 3 to 4°C in April and 4.5 to 6°C in May and June, and the salinities were adjusted to 25‰.

Table 8 presents the LC₅₀ (EC₅₀) values expressed as ppm-h for the stage I larvae of five marine species. Rice et al., (1981) observed that larvae that could not swim at the end of the 4-day exposure would subsequently die. Thus, they used inability to swim (not actual mortality) to determine EC₅₀ values. Also shown are the mean LC₅₀ values for 13 bioassays of pink salmon fry and 5 bioassays of adult kelp shrimp.

TABLE 8: Static Bioassay LC₅₀ Values for Stage I Larvae of Several Species of Marine Organisms, and for Pink Salmon Fry and Adult Kelp Shrimp

<u>Species</u>	<u>Number of bioassays</u>	<u>Total aromatics,^{a,b} ppm 96 hr LC₅₀</u>	<u>Exposure in ppm-h^c</u>	
			<u>24 hours</u>	<u>96 hours</u>
<u>Larvae</u>				
King crab	3	2.10 ± 0.60	38	202
Coonstripe shrimp	5	1.78 ± 0.24	32	171
Kelp shrimp	2	0.80 ± 0.57	14	77
Dungeness crab	1	1.7	31	163
Pacific herring	2	2.0 ± 0.85	36	192
<u>Fry and Adults</u>				
Pink salmon fry	13	1.93 ± 0.65	35	185
Kelp shrimp adults	5	1.80 ± 1.10	32	173

^a ppm total dissolved aromatic hydrocarbons (saturate hydrocarbons were not measured).

^b The LC₅₀ is based on number of larvae unable to swim (not mortality) after 96 h exposure, thus EC₅₀.

^c Solution was renewed daily. Thus, exposure was calculated as concentration in ppm (96 h-LC₅₀) x 0.75 (evaporation loss was 0.25) x 24 or 96 h.

The data in Table 8 show that kelp shrimp larvae were about two times as sensitive to dissolved hydrocarbons than were adult kelp shrimp. Pacific herring larvae were less sensitive to dissolved hydrocarbons from ballast water (36 ppm-h, Table 2) than were adult herring to dissolved hydrocarbons from Cook Inlet crude oil (22 ppm-h, Table 7). King crab larvae were about twice as sensitive as adults (38 vs 66 ppm-h). Pink salmon fry had about the same sensitivity in both waters, 30 and 35 ppm-h, Tables 7 and 8. Adult kelp shrimp also had the same response (32 and 33 ppm-h) showing that the exposure waters apparently contained the same relative amounts of dissolved constituents.

University of Alaska, Fairbanks

Morrow et al. (1975) determined the 24 h to 96 h LC₅₀ values of young coho salmon exposed to a number of individual hydrocarbons found in the WSF of crude oils. The exposure water salinities were 30‰ and the temperature was kept at 8°C. The average fish weight was about 5 g each in the fall of the year to almost 40 g each in May.

The addition of 100 ppm equivalent of each hydrocarbon to individual aquaria did not produce mortalities in 4 days for pentane, hexane, heptane, octane, cyclopentane, ethylcyclopentane, cyclohexane, and ethylcyclohexane. In all cases, this addition exceeded the solubility of the hydrocarbon in water (McAuliffe, 1968), so there was excess separate phase hydrocarbon present, at least initially. The 95 L aquaria were covered with a glass plate so that evaporation would have been reduced, but biodegradation could have occurred. The fish did show signs of mild irritation to the normal alkanes (pentane, hexane, heptane, and octane). These consisted of rapid, erratic movement and "coughing." No noticeable alterations of behavior were found with exposure to the cycloalkanes. The aromatic hydrocarbons benzene, toluene, xylene, and ethylbenzene, at 20 to 100 ppm, all produced within 15 to 20 min, rapid, violent, and erratic swimming. The fish dashed about the aquaria, leaped out of the water, crashing against the cover and sides of the tank. This was followed by "coughing," loss of equilibrium, and death. Fish that survived the first few hours of exposure generally survived to the end of the 96 h exposure.

An estimated 24 h LC_{50} expressed as ppm-h for benzene, toluene, xylene, and ethylbenzene are 960, 600, 720, and 600 respectively. If most of the mortality occurred during the first few hours, the 4 h exposure would be 160, 100, 120, and 100 ppm-h.

OTHER BIOASSAYS

Caldwell et al. (1977) measured the effects of the WSF of Cook Inlet crude oil and its major aromatic components on larval stages of the Dungeness crab, cancer magister Dana. Table 9 summarizes the 24 and 48 h exposures expressed as ppm-h. The data show that the first instar zoeae is not very sensitive to the C_1 to C_{10} WSF of Cook Inlet crude oil nor to individual aromatic hydrocarbons. The data do show that the methyl substituted benzenes, and the naphthalenes to be more toxic than benzene. Increased toxicity with increase or in carbon numbers or equal molar concentrations of saturate and aromatic hydrocarbons have also been shown on the photosynthesis of two algae species, Hutchinson et al. (1979). Other bioassay studies using individual hydrocarbons have been summarized by Rice et al. (1977).

With the exception of toluene, often being present in higher concentration in crude oils than benzene, the concentration of aromatic hydrocarbons decrease with increased in carbon number. The solubility of individual aromatic hydrocarbons also decrease with increasing carbon number (Anderson et al., 1974; McAuliffe, 1979). Thus, the biological toxicity from hydrocarbons in solution probably resides principally in the more prevalent and soluble lower molecular weight hydrocarbons, and in particular the aromatic hydrocarbons.

Carr and Reish (1977) found six polychaete species to be relatively resistant to the WSF of C_1 to C_{10} hydrocarbons in 4-day exposures, the shortest time measured in 28-day tests (Table 10). The 28-day LC_{10} values were only slightly lower than the 4-day LC_{50} values.

Struksaker et al., (1974) found benzene to be relatively non-toxic to eggs and larvae of Pacific herring and Northern Anchovy in 24 h exposures. The results

TABLE 9: Bioassay of the Seawater-Soluble Fraction of Cook Inlet Crude Oil and its Major Aromatic Components on the First Instar Zoeae of the Dungeness Crab, Cancer Magister Dana^a

Oil or Hydrocarbon	Exposure in ppm-h ^b	Exposure in ppm-h ^b
	24 hours	48 hours
Cook Inlet crude oil (C ₁ to C ₁₀ fraction)	60	120
Benzene	6,250	12,500
Toluene	3,050	6,100
Ethylbenzene	720	1,440
m-xylene	595	1,190
o-xylene	680	1,360
1, 2, 4-trimethylbenzene	305	610
1, 3, 5-trimethylbenzene	235	470
1, 2, 4, 5-tetramethylbenzene	>95	>190
Naphthalene	>63	>125
1-methylnaphthalene	147	295
2-methylnaphthalene	90	180

^aCaldwell et al., 1977. Bioassay water temperature was 13°C, salinity 30‰ seawater. At least 50 larvae were used per test concentration. Solutions were changed each 24 hr.

^bppm-hr calculated as 75% of the initial concentration.

TABLE 10: Bioassays of Polychaetous Annelids with the Water Soluble Fraction of South Louisiana Crude Oil and No. 2 Fuel Oil

Polychaetes	Exposure as ppm-hr (LC ₅₀ x 96 h)	
	S. La Crude Oil	No. 2 Fuel Oil
<u>Ctenodrilus serratus</u>	>1900	355
<u>Ophryotrocha</u> sp.	1240	280
<u>Ophryotrocha pueriles</u>	1650	210
<u>Capitella capitata</u>	>1900, 1150 ^a	>835, 220 ^a
<u>Cirriformia spirabranca</u>	>1900	>835
<u>Neanthes arenaceodentata</u>	1200	260

^aRossi et al., 1976; Rossi and Anderson, 1976; all other values from Carr and Reish, 1977. Filtered seawater at 19.5°C.

were: (a) Herring larvae mortality was >648 ppm-h for larvae hatched from eggs exposed for 24 h immediately after fertilization; there was no increase in abnormal larvae at 225 ppm-h exposure, but a significant increase in abnormal larvae occurred at 648 ppm-h; (b) herring larvae mortality 7 days after exposure was >348 ppm-h for larvae that were exposed for 24 h on day 2 or 3 after hatching; and (c) anchovy larvae mortality for 6-day-old larvae that were exposed for 24 h on the day after hatching was >770 ppm-h.

HYDROCARBONS IN WATER UNDER FIELD OIL SLICKS

The extensive studies cited before have measured exposures to WSF of crude oils (and some refined products) and to individual hydrocarbons that cause mortality or behavioral changes. These can now be compared with field exposures of dissolved hydrocarbons.

Total hydrocarbons have been measured in water under field research oil slicks, and under slicks from accidental spills. It is possible to estimate expected concentrations by knowing the average thickness of the surface slicks.

Oil Slick Thickness

If the amount of oil discharged is known and the area of the slick measured, an average oil thickness can be calculated.

During API-EPA research oil spills, 3.2 m³ (20 bbl) of three different oils (24 to 39° API gravity) were released. After 15 to 30 min, the area of these slicks at the start of aerial spraying was 2 to 3 hectares (5 to 7.5 acres) measured from aerial photographs (Johnson et al., 1978; McAuliffe et al., 1980, 1981). The average thickness was therefore 0.1 to 0.2 mm, but decreased during the 30 min it took to spray the slicks.

During the Gulf of Mexico platform spill, from 240 to 950 m³ (1500 to 6000 bbl) of oil flowed from the wells each day. Although the observed slick size varied with weather conditions, its general size was 1 km wide and 10 km long, (0.6 to 6 mi) with the thicker oil near the platform (McAuliffe et al, 1975; Murray, 1975). The average thickness was from 0.02 to 0.09 mm.

A well on Bravo Platform in the Ekofisk oil field blew out April 22, 1977 and flowed oil for 7.5 days at an estimated rate of 2,800 m³ (17,600 bbl)/d. Audunson (1978) calculates that the maximum oil on the surface at the end of oil discharge was 5,500 m³ (9,300 bbl), thereafter decreasing. During the discharge, a continuous slick, estimated to be 1 mm thick, was about 100 to 200 m wide and about 1 km long. At the edge of this continuous slick, the oil started forming thicker areas of yellowish-brown water-in-oil emulsions (mousse) containing from 50 to 70% water. The maximum area of the thick part of slick was estimated to be 500 km² containing the 5,500 m³ of oil. The average oil thickness was therefore 0.01 mm.

A 750 bbl research spill of Statfjord crude oil was released July 25, 1982, in the North Sea about 160 km off the Norwegian coast (Audunson et al., 1984). The

oil was released over a 2 h period corresponding to a well blowout release of 1500 m^3 (9,000 bbl)/d. The thick part of the slick containing 90% of the oil, attained an area of 100 hectares after 8 h and remained between 150 and 200 hectares for the next 5 days. During this time, the volume of oil decreased from 60 m^3 (380 bbl) to 20 m^3 (120 bbl). Thus, the average spill thickness decreased from 0.06 mm to 0.013 mm.

There are conditions that can produce slicks with average thickness more or less than 0.1 mm. A large release over a short time can initially give thick slicks near the release point. For example, the release of $30,000 \text{ m}^3$ in 1 h from a tanker could produce a downcurrent slick that might be 20 mm thick at 100 m from the source, 5 to 7 mm thick at 1 km, thereafter thinning to the average of about 0.1 mm.

Conversely, a subsurface release from a well blowout produces a thinner slick. This results from the entrainment of water (and oil) in the rising gas bubbles. When the rising plume becomes fully developed a considerable quantity of water is pumped to the surface. Near and at the surface, the water and oil flow away from the center of the plume and the oil slick spreads at a faster rate than oil released on the surface. The model of Fannelop and Sjoen (1980) estimates that at 1 km from a 4800 m^3 (30,000 bbl)/d subsurface discharge the slick thickness is 0.06 mm, and for a 320 m^3 (2,000 bbl)/d release, the thickness is 0.01 mm. The corresponding thicknesses for a surface discharge would be 1.3 and 0.09 mm, respectively.

The Ixtoc 1 well in the Gulf of Mexico from June 3, 1979 until the well was killed by relief wells March 23, 1980, released an estimated $500,000 \text{ m}^3$ of crude oil from the top of the blowout preventer (12 m above seafloor) in 50 m of water. The initial flow was estimated to be about $4,800 \text{ m}^3$ /d during June and July (Annon, 1980). Jernolov and Linden (1981) state that during the initial flow, the slick was 0.7 - 5 km wide and 60 km long. If the slick was 3 km wide, 60 km long, the current was 0.5 kn, and the release rate was 4800 m^3 (30,000 bbl)/day, the average slick thickness was 0.07 mm.

Oils have different spreading tendencies, particularly on cold water (Tramier et al., 1981). Thus, in the arctic with waters near freezing, some spilled oils may have an average thickness of more than 0.1 mm, perhaps 2 to 3 mm, but this has not been demonstrated on open water with wind, waves, and currents.

Total Oil Measured Under Research Oil Slicks

If oil slicks generally have an average thickness of 0.1 mm, the highest concentration of oil uniformly mixed in the top metre of water would be $100 \mu\text{L/L}$ (ppm), 10 ppm if mixed through 10 m, if the slick was immediately and completely dispersed chemically. Natural dispersion produces much lower oil concentrations in the underlying water.

These concentrations have not been attained in field research oil spills, although approached. Aircraft sprayed La Rosa and Murban crude oil slicks off New Jersey. The highest concentrations measured in the first samples collected 20 to 25 min after spraying were 2-3 ppm at 1 and 3 m, and 0.5 ppm at 6 m

under the La Rosa treated slick estimated to have been half dispersed (McAuliffe et al., 1980). Concentrations of 1 to 1.5 ppm persisted at 1 and 3 m through 100 min. Oil concentrations under the Murban slick estimated to have been 90 to 95% dispersed were 18 ppm at 1 m, 10 ppm at 3 m, 23 min after spraying. After 50-57 min, the concentrations were 3-4 ppm at 1 m, 3 ppm at 3 m, and 1 ppm at 6 and 9 m.

For the best dispersed (approximately 80%) Prudhoe Bay crude oil slick in research studies off southern California, McAuliffe et al., (1981) measured total oil concentrations 15 min after aircraft spraying of 30-50 ppm at 1 m, 10 ppm at 3 m; 54 min after spraying the concentrations were 12-14 ppm at 1, 3 and 6 m, and 2 ppm at 9 m. After 3 h 40 min, the concentrations at 1, 3, 6, and 9 m were 1, 2.3, 1, and 0.5 ppm, respectively.

Cormack and Nichols (1977) measured concentrations of Ekofisk crude oil chemically dispersed at 1 m ranging from 16 to 48 ppm within the first 2 min after boat spraying, 5 to 18 ppm from 5 to 10 min after spraying, decreasing to 1 to 2 ppm after 100 min.

Aerially sprayed Statfjord crude oil slicks were sampled 30 to 50 min later. The highest concentrations measured were 40, 32, 25, and 4 ppm at 0.5, 1, 2, and 3 m depths (Lichtenthaler and Daling 1985). Water samples collected 165 to 225 min after spraying contained 1.2, 0.2, 0.1, and 0.7 ppm oil at 0.5, 1, 2, and 3 m. The measured oil concentrations at 1 m under two untreated slicks ranged from 0.25 to 5 ppm (mean of 8 samples was 1.72 ± 1.67); at 2 m the range was 0.03 to 0.63 (mean of 8 samples was 0.22 ± 0.23).

Other field research oil spill studies using chemical dispersants have measured lower concentrations of oil in underlying water.

EVAPORATIVE LOSS OF VOLATILE HYDROCARBONS (WEATHERING)

Because oil slicks are generally thin on average (0.1 to 0.01 mm), the concentration of oil that can be dispersed into underlying water is usually restricted to less than 100 ppm in the top metre of water. The thin slick and small diameter of dispersed oil droplets allows the volatile hydrocarbons (C_1 to C_{10}) to quickly evaporate and go into solution. Evaporation greatly predominates over solution. McAuliffe (1971, 1974) demonstrated this relationship in laboratory studies. Harrison et al., (1975) incorporated the concept in a mathematical model and predicted that for aromatics, evaporation would be one hundred times faster than solution; for alkanes, ten thousand times faster. The biological toxicity of the remaining surface oil or oil droplets dispersed into the water column is thereby greatly reduced.

Estimated loss of volatile hydrocarbons has been presented by van Oudenhoven et al., (1983), based on an evaporative model (Nadeau and Mackay, 1978; Mackay et al., 1980), for a range of different specific gravity crude oils. About half of the evaporative loss occurs by 12 h.

Field measurements have demonstrated the rapid loss and low concentrations of C_1 to C_{10} hydrocarbons in oil samples collected from surface slicks, and in water under untreated and chemically dispersed crude oil slicks. McAuliffe

(1977) and Johnson et al., (1978) showed the complete loss of low-molecular-weight aromatic hydrocarbons in 8 h from oil samples collected from a slick following the release of 24° API gravity crude oil - benzene and toluene within 1 h, dimethylbenzenes by 5 h, and trimethylbenzenes (C₉) by 8 h.

Of the 68 water samples collected up to 8 h after the oils were released, C₁ to C₁₀ hydrocarbons were found in only the first five collected 15 to 18 min after oil release. The total C₁ to C₁₀ hydrocarbons under the light Murban crude oil slick were 60, 16, and 5 ppb for the 1.5 m samples, a single 10 m sample contained 2.4 ppb. Only one sample at 1.5 m under the more viscous La Rosa slick contained 6 ppb.

Under chemically dispersed Murban and La Rosa crude oil slicks, low total C₁ to C₁₀ hydrocarbons were measured (McAuliffe et al., 1980). Forty-six minutes after dispersant spraying, total C₁ to C₁₀ hydrocarbons were 40, 12, 5, 4, and 1 ppb for surface, 1, 3, 6, and 9 m samples. One metre samples under the 90 to 95% chemically dispersed Murban slick contained 46, 12, and 2 ppb at 18, 46, and 110 min after dispersant spraying. Samples from under the 50% dispersed La Rosa slick contained after 47 min 14 ppb in the surface sample, and 12 ppb at 3 m. After 94 min, the surface sample contained 9 ppb, the 3 m sample 5 ppb.

The most complete set of data were obtained for the Prudhoe Bay research oil spills off southern California (McAuliffe et al, 1981; McAuliffe, 1985). Figure 4 is a plot of total C₁ to C₁₀ hydrocarbon concentrations measured in water samples associated with the best chemically dispersed slicks. The highest concentrations were found in samples collected from 10 to 60 min after the end of dispersant spraying. The mean concentrations in ppb from 10 to 30 min by depth are: 1 m, 42 ± 47 , n = 6; 3 m, 54 ± 77 , n = 6; 6 m, 33 ± 46 , n = 3, and 9 m, 66, n = 1. The mean for all depths during the 10 to 30 min period is 46 ± 56 , n = 16. The mean concentrations from 30 min to 1 h are: 1 m, 29 ± 28 , n = 4; 3 m, 14 ± 8 , n = 4; 6 m, 12 ± 11 , n = 3, and 9 m, 3.7 ± 4.7 , n = 2. The mean for all samples collected from 30 min to 1 h for all depths is 16 ± 18 , n = 13.

As shown in Figure 4, the concentrations of total C₁ to C₁₀ hydrocarbons are fairly uniformly distributed in the top 6 m of water, although 1 and 3 m samples are higher. Only two of the 9 m samples had concentrations greater than 10 ppb. The curve shown in Figure 4 has been drawn through the mean point for the first 30 min, the second 30 min, and the mean of concentrations at 3-4 h and around 6 h. The area under the curve estimates the exposure for 24 h as 0.06 ppm-h.

The total C₁ to C₁₀ hydrocarbon fraction under untreated Prudhoe Bay crude oil slicks ranged from 1 to 3.5 ppb (mean 1.6) in the top 3 m of water in samples collected from 15 to 30 min after the oil was discharged. The 24 h C₁ to C₁₀ exposure is about 0.002 ppm-h (only background concentrations were detected after 30 min). Because of evaporation, dissolved hydrocarbons are highest near the crude oil release point. Thus, the volumes of affected waters are relatively small compared to the total area of the slick.

COMPARISON OF FIELD AND LABORATORY EXPOSURES TO TOTAL C₁ TO C₁₀ HYDROCARBONS

The above discussion on oil spill slick thickness and weathering of crude oils shows that the concentration of total oil in water is relatively low, and the weathering of the oil is relatively rapid. Thus, organisms are exposed to transitory effects from dissolved hydrocarbons.

Table 11 compares the total C₁ to C₁₀ exposures in ppm-h for the field research oil spills with the exposures found to cause organism mortality or behavioral changes in laboratory experiments. Exposures in ppm-h are for 24 h unless otherwise indicated in Table 11 by enclosing other times in parentheses. Most of the studies are for subarctic and northern Pacific species.

The first line of Table 11 shows the 24 h exposure organisms received in water under untreated Prudhoe Bay crude (PBC) oil slicks, and in chemically dispersed plumes of PBC oil as discussed in the previous section. All data in Table 11 are exposures required to cause 50% mortality, except the salmon homing studies and the hatching success of herring eggs.

The chum salmon half-kill value of 19 ppm-h is similar to the 30 ppm-h value for juvenile pink salmon to the WSF of Cook Inlet crude oil, and the 35 ppm-h for pink salmon measured with Port Valdez ballast water, Tables 7 and 8.

The half-kill value for chum salmon fry to the dissolved hydrocarbons from dispersed PBC oil was 9 ppm-h. This demonstrates that the fry were about twice as sensitive to the C to C fraction of dispersed oil compared with the WSF from untreated PBC oil. The chum fry were only slightly more sensitive to dispersed oil than were adult coho salmon, 9 vs 12 ppm-h. These exposures to cause half-kill are 150-200 times higher than the measured field exposure. The salmon bioassay with Prudhoe Bay crude oil show these organisms to be among the most sensitive of all those reported in this paper.

The exposures that had no effect on chinook homing in fresh water and coho homing in seawater from the WSF of untreated PBC oil and chemically dispersed oil were from 15 to 135 times higher than observed for open water field exposures.

High exposures (from >9,500 to >113,000 times field exposure) of herring eggs to the WSF of PBC oil before, during, and for 24 hrs after fertilization had no effect in percent eggs hatching, time to hatch (12 to 13 days after fertilization), or to increased abnormalities in hatched larvae.

The exposure concentrations of the water soluble fraction (WSF) of crude oils, or individual hydrocarbons in laboratory studies to cause one half mortality of the various test organisms are very much higher than measured in the field studies - from 8,000 to over 6 million times higher.

Only a few bioassay studies with chemically dispersed oil have measured the water soluble fraction in the exposure waters. Thus, the last column in Table 11 is blank for most of the species. An estimate can be made using the limited data. The field research studies show the total C₁ to C₁₀ dissolved hydrocarbons to be 30 times higher in the dispersed oil plume compared with the concentrations under untreated crude oil slicks (0.060/0.002). The chum

TABLE 11: Comparison of Measured Dissolved Hydrocarbons in Sea Trials with Those Observed in Laboratory Behavioral and Mortality Studies. All Exposures are 24 Hours Unless a Different Time is Shown in Parenthesis.

Study	Dissolved Hydrocarbons		Number of Times Sea Trial Exposures Would Need to be Increased to Give the Same Exposures as Laboratory Studies	
	Exposure in ppm-h		Untreated Oil	Chemically Dispersed Oil
	Untreated Oil	Chemically Dispersed Oil		
Organism and Fresh Crude Oil or Hydrocarbons Used				
<u>Prudhoe Bay Crude (PBC) Oil</u>				
1979 California Field Trials	0.002	0.060		
<u>Salmon Homing, PBC Oil</u>				
Chinook in fresh water	0.27(1h)	1.50(1h)	135	25
Coho in seawater	0.07(1h)	0.90(1h)	35	15
<u>Salmon Bioassays, PBC Oil</u>				
Coho Adults	>5(4h)	12(4h)	>2500	200
Chum Fry	19	9	9500	150
<u>Herring Eggs, PBC Oil</u>				
Hatching Success,				
Before fertilization	>19(2h)		>9500	
During fertilization	>19(2h)		>9500	
Percent hatching	>227		>113,000	
Time to hatch	>227		>113,000	
Increased abnormal larvae	>227		>113,000	
<u>Port Valdez Ballast Water</u>				
King crab larvae	38		19,000	
Coonstripe shrimp larvae	32		16,000	
Kelp shrimp larvae	14		7,000	
Dungeness crab larvae	31		15,500	
Pacific herring larvae	36		18,000	
Pink salmon fry	35		17,500	
Kelp shrimp adults	32		16,000	

TABLE 11: Comparison of Measured Dissolved Hydrocarbons in Sea Trials with Those Observed in Laboratory Behavioral and Mortality Studies. All Exposures are 24 Hours Unless a Different Time is Shown in Parenthesis. (Cont'd)

Study	Dissolved Hydrocarbons		Number of Times Sea Trial Exposures Would Need to be Increased to Give the Same Exposures as Laboratory Studies	
	Exposure in ppm-h		Untreated	Chemically
Organism and Fresh Crude Oil or Hydrocarbons Used	Untreated Oil	Chemically Dispersed Oil	Oil	Dispersed Oil
<u>Cook Inlet Crude Oil</u>				
39 species of fish, crustaceans, echinoderms, mollusks, annelids, and nemerteans.	16 to >221		8,000 >110,000	
Juvenile pink salmon	29		14,500	
Dungeness crab, first instar zoeae	120(48h)		60,000(48h)	
<u>South Louisiana Crude Oil</u>				
Six polychaete species,	1200 to >1900 (96h)		600,000 to >950,000(96h)	
<u>Individual Hydrocarbons</u>				
<u>Juvenile pink salmon</u>				
Naphthalene	29		14,500	
<u>Young coho salmon</u>				
Saturate hydrocarbons- nC ₅ , -C ₆ , -C ₇ , -C ₈ , cyclo C ₅ , ethylcyclo C ₅ , cyclo C ₆ , and ethylcyclo C ₆	>2400		>1.2x10 ⁶	
Aromatic hydrocarbons benzene, toluene, xylene, and ethylbenzene	600 to 960		300,000 to 480,000	
<u>Dungeness crab, First instar zoeae</u>				
Benzene, toluene, C ₂ -benzenes, C ₃ -benzenes, and naphthalenes	180 to 12,500		90,000 to 6.25x10 ⁶	
<u>Pacific herring and Northern anchovy eggs and larvae</u>				
Benzene	225 to >770		113,000 to >385,000	

salmon bioassays concentrations for dispersed oil were about one-half that for the WSF of untreated oil. Therefore a value 60 times lower can be estimated for chemically dispersed oil for the other organisms in the last column of Table 11. An approximation can be made by dividing the values for untreated oil in the next to the last column by 100. This approximation indicates that chemically dispersing oil slicks will produce exposures that are many times lower than those estimated to cause mortality in the many species in Table 11 including many subarctic species.

Planktonic organism in near surface waters may move with the dispersed oil plume and receive the greatest exposure. However, even assuming that there would be mortality, a measurable effect will not be observed. Most of these planktonic organisms have short life cycles and are produced in very large numbers. They are often limited by their food supply. If killed, they are replaced by others from outside the affected volume of water.

These extensive studies show that it is highly unlikely that a crude oil spill or the chemical dispersion of the slick will cause mortality of marine organisms in the water column or in bottom sediments. There should be no effects, for example, on either juvenile or adult salmon. Only chemical dispersion of fresh oil in shallow water (less than 3m) with poor water exchange is there a possibility of an adverse effect.

SUMMARY AND CONCLUSIONS

Toxicity of crude oils to aquatic organisms is thought to reside principally in the low-molecular-weight ($< C_{12}$) hydrocarbons. These soluble/volatile hydrocarbons in water in equilibrium with an excess of crude oil total from 20 to 40 ppm and are about equally divided between saturate (alkane and cycloalkane) and aromatic hydrocarbons. Benzene and toluene constitute from 70 to 85% of the aromatic hydrocarbon fraction.

A large number of behavioral and mortality (bioassay) studies have been conducted with the water-soluble fraction (WSF) of oils. A lesser number have used chemically dispersed oil. Many have measured the dissolved C_1 to C_{10} hydrocarbon fraction, or the dissolved low-molecular-weight aromatic hydrocarbons. From these studies an exposure or dose can be calculated (i.e., LC_{50} concentration times the time of exposure) and expressed in mg/L-hours (ppm-h).

Reported here are mortality studies for about 50 species with exposures to cause half-kill ranging from 9 ppm-h (chum salmon fry exposed to chemically dispersed Prudhoe Bay crude oil) to $> 1,900$ ppm-h (3 species of polychaetes exposed to the WSF of a South Louisiana crude oil).

Larval stages of organisms were no more than twice as sensitive to the WSF of crude oil compared with adults. The kelp shrimp larvae was the most sensitive at 14 ppm-h for half-kill.

Limited studies indicate that chemically dispersed crude oil is about twice as toxic as the WSF of crude oils based upon the total C_1 to C_{10} hydrocarbon exposures using chum salmon fry.

Chinook salmon homed successfully and without apparent effect in fresh water and coho salmon in seawater, after exposure to 0.9 to 1.5 ppm-h of chemically dispersed Prudhoe Bay crude oil.

Exposure to > 19 ppm-h of WSF of Prudhoe Bay crude oil before or during fertilization had no effect on Pacific herring percent egg fertilization. Exposure to > 227 ppm-h had no effect on the percent eggs that hatched, the time to hatch, or on larval abnormalities.

Oil slick thickness after an hour or two on waters range from 0.1 to 0.01 mm and are relatively independent of spill size. Thus, the total oil completely dispersed and mixed in the top metre of water ranges from 10 to 100 ppm, 1 to 10 ppm if mixed uniformly in the top 10 m. Field research spills have shown the following maximum concentrations: 40-50 ppm in the top metre, 10 to 15 ppm in the top 6 m, 2.5 ppm at 9 m.

The total C₁ to C₁₀ dissolved hydrocarbons under untreated crude oil slicks ranged from 1 to 3.5 ppb in the top 3 m of water and thereafter decreased (an exposure for 24 h of 0.002 ppm-h).

The total C₁ to C₁₀ hydrocarbons in the best chemically dispersed crude oil plumes were about 150 ppb for the first 30 min, followed by rapid loss by evaporation and/or dilution (an exposure for 24 h of 0.060 ppm-h).

The measured field exposures to C₁ to C₁₀ hydrocarbons from untreated and chemically dispersed crude oils are much lower (from 150 to over a million times lower) than those observed to kill a wide range of organisms in laboratory bioassays. Thus oil spills and chemical dispersion of crude oil slicks are unlikely to have an adverse effect on larval, juvenile, or adult marine organisms.

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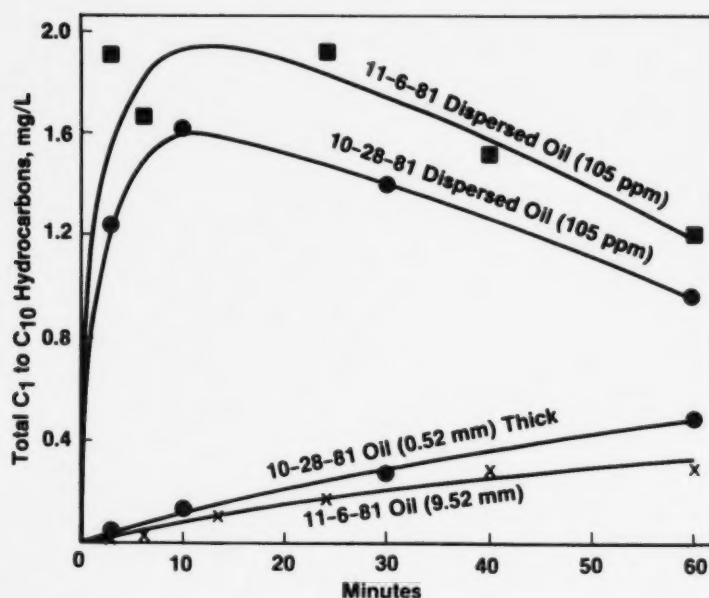


Figure 1: Chinook salmon homing experiment. Total C_1 to C_{10} hydrocarbons in waters to which salmon were exposed to untreated and chemically dispersed Prudhoe Bay crude oil.

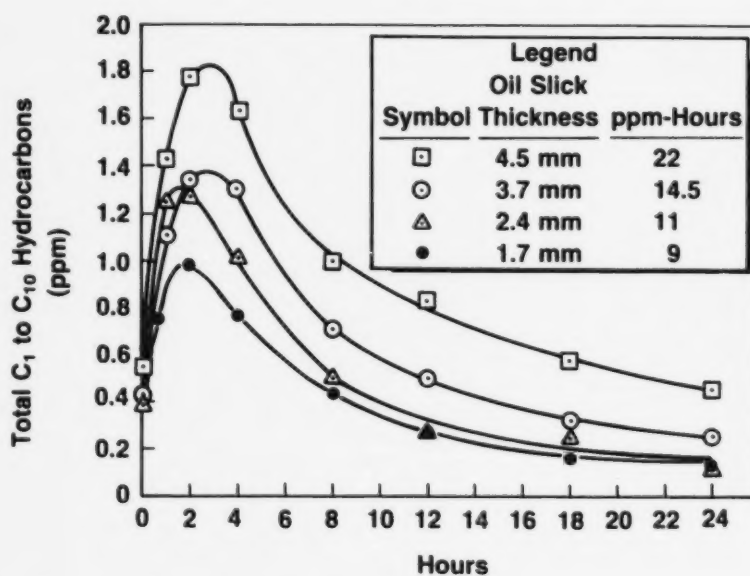


Figure 2: Chum salmon fry bioassay. Total C_1 to C_{10} hydrocarbons in exposure water under fresh Prudhoe Bay crude oil slicks.

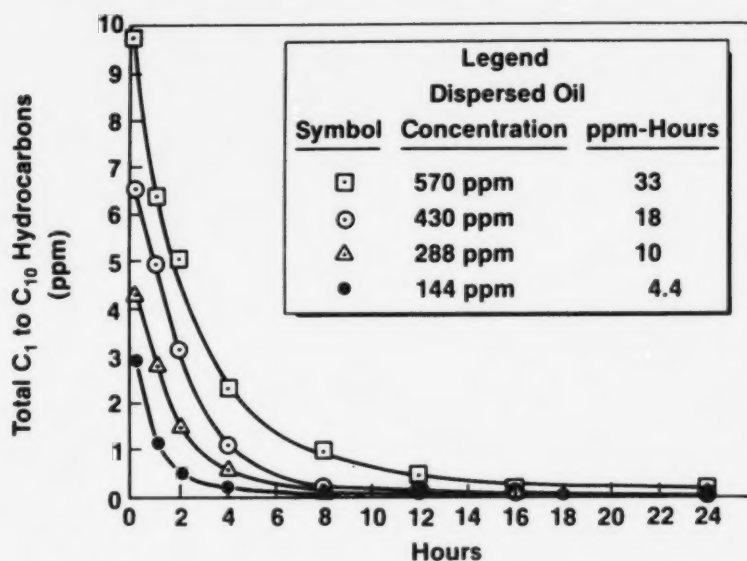


Figure 3: Chum salmon fry bioassay. Total C_1 to C_{10} hydrocarbons in chemically dispersed Prudhoe Bay crude oil exposure waters.

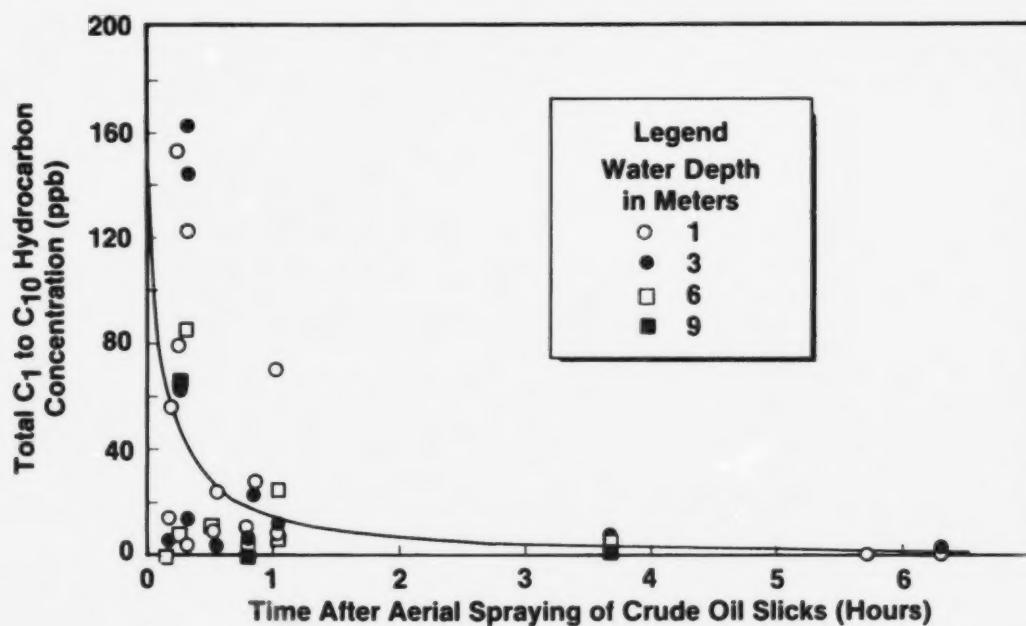


Figure 4: Total C_1 to C_{10} hydrocarbons in the dispersed oil plumes following aerial spraying of Prudhoe Bay crude oil research slicks.

LARGE-SCALE LABORATORY STUDIES OF DISPERSANT EFFECTIVENESS, APPLICATION, AND MIXING

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INTRODUCTION

This paper reviews three separate studies, funded by the Environmental Studies Revolving Funds (ESRF), which investigate the effectiveness of chemical dispersants on oil. Each of the projects involved large-scale laboratory testing programs which were conducted in our facility in Ottawa. The three studies are:

1. Effectiveness of the Repeat Application of Chemical Dispersants on Oil (ESRF 006);
2. Development of a High Pressure Water Mixing Concept for Use with Ship-Based Dispersant Application (ESRF 034); and
3. Meso-Scale Laboratory Dispersant Effectiveness Testing (In Preparation).

Test Facility

All of the laboratory work for these studies was conducted in the test tank shown in Figures 1 and 2. The tank is 11 metres long, 1.2 metres wide and 1.2 metres deep and can be used with or without the overhead wind tunnel and/or a variable speed wave paddle. Dispersant spray booms, mixing systems and other measuring equipment are towed over the top of the tank by a motorized tow cable and cart running along a linear bearing. Cart speeds ranging from 0 to 3+ m/sec, waves up to 0.3 metres high and wind speeds up to 10 m/s are attainable with the present equipment.

Dispersant can be applied to the tank surface either by an overhead boom or by nozzles mounted on the moving cart for those tests where the wind tunnel is in use.

Water samples for dispersed oil concentration measurement can be taken from the 5 sampling tubes located in the centre of the tank (see Figure 1). Oil concentrations are measured by extracting the oil from the water using a colourless solvent and then determining the extracted oil quantity with a UV/VIS spectrophotometer. Water can also be drawn off at these locations and passed through small cells where photographs are taken to record the drop-size of any dispersed oil.

For more detailed descriptions of the test equipment and experimental methods used in the three studies the reader is referred to the final reports available from ESRF.

Study #1: Effectiveness of the Repeat Application of Chemical Dispersants on Oil

When a chemical dispersant is applied to an oil slick and only partially removes the oil from the surface, it is important to know, during a countermeasures operation, whether a second application will be effective in dispersing the remaining oil. It is possible that dispersant application subsequent to the first will not be effective due to chemical property differences in the remaining surface oil or in the resurfaced oil. To determine the validity of this suggestion, large-scale laboratory tests were executed in which oil slick dispersal efficiencies were measured after the first and second dispersant applications.

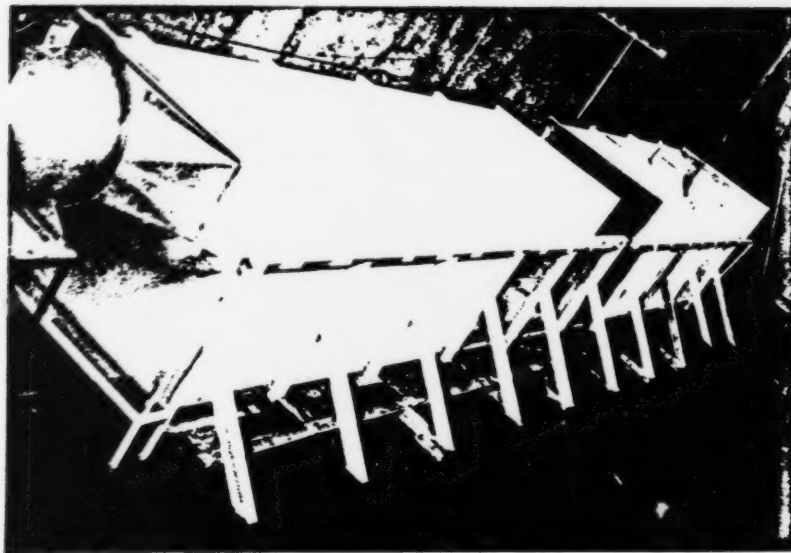


FIGURE 1 TEST TANK WITH WIND TUNNEL IN PLACE

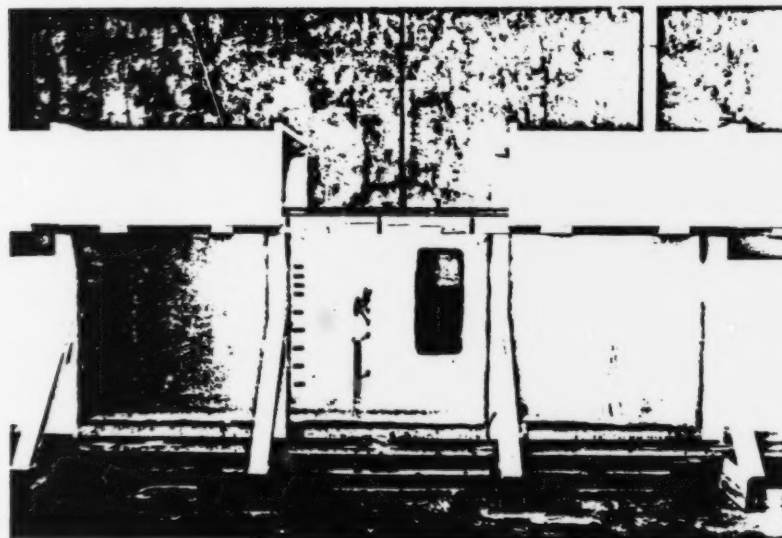


FIGURE 2 CENTRE SECTION OF TEST TANK SHOWING
OBSERVATION WINDOWS

Test Methodology and Conditions

Two test procedures were used in the study. The first test sequence was designed to simulate the simple process of oil being initially "dispersed", then being allowed to completely resurface to be hit again by dispersant. The second procedure was similar but included the addition of a mixing energy to the water in the test tank. This turbulence was added to suspend a portion of the oil, dispersed by the first application, in the water column. A more detailed test methodology is outlined below.

- Step 1: Oil was applied to the water surface in the test tank.
- Step 2: Immediately prior to the first application of dispersant, a surface sample of oil and water was taken to determine the oil's density, viscosity, and surface tension characteristics.
- Step 3: Dispersant was applied to the oil and the mixture agitated by a high-pressure water jet mixing system. The use of this system to generate the dispersion provided a very high level of control on the mixing energy and hence, on the resulting dispersion.
- Step 4: The efficiency of the initial dispersion was measured by taking water samples for oil concentrations and photographing oil droplets for drop size distributions immediately after the dispersion.
- Step 5: The dispersed oil was allowed to re-surface after the dispersion and the apparatus was readied for the second application.

- or for procedure II -

- Step 5: A background level of mixing was applied to the water in the tank to hold the smaller of the dispersed oil drops in suspension in the water.
- Step 6: Twenty to thirty minutes after the time of the initial dispersion another surface sample of oil and water was taken for oil density, oil viscosity, and surface tension measurements.
- Step 7: The second application of dispersant was applied, followed by the same level of mixing energy.
- Step 8: The efficiency of the second dispersion was recorded.

A total of seven large-scale tests were conducted; four where the oil was allowed to re-surface, and three with background mixing of the water in the test tank. The initial conditions used in the testing program are listed below.

* Water temperature	1° - 5°C
* Air temperature	15°C
* Oil type	Alberta Sweet Mixed Blend Crude
* Initial oil thickness	0.5 mm
* Dispersant type	COREXIT 9527
* Dispersant application	1:100
* Dispersant drop size	Constant: = 750 um volume median diameter
* Mixing energy	High pressure water: 1000 psi, 4 gpm
* Background mixing level (for Procedure II)	Constant: provided by recirculating pump and diffuser piping.

Test Results

For all the tests conducted, the results show that both the quantity of oil dispersed (Figures 3 and 4) and the size distribution of the oil drops generated (Figure 5 and 6) by the second application and mixing sequence were similar to, or better than, those from the initial application of dispersant. Therefore, it appears that the second or repeat application of dispersant is as effective as the first, at least under the conditions present in this study.

Measurements of oil properties taken during the study indicate that the first application of dispersant did not significantly change either the oil's density or its viscosity (see Table 1) but that there occurred a 75-85% reduction in the oil-water interfacial tension just prior to the second application. Some dispersant therefore remained in the re-surfaced or undispersed oil. The results indicate that the presence of this surfactant neither reduced the effectiveness of the second application nor did it greatly improve the second dispersion.

Study #2: Development of a High Pressure Water Mixing Concept for Use with Ship-Based Dispersant Application

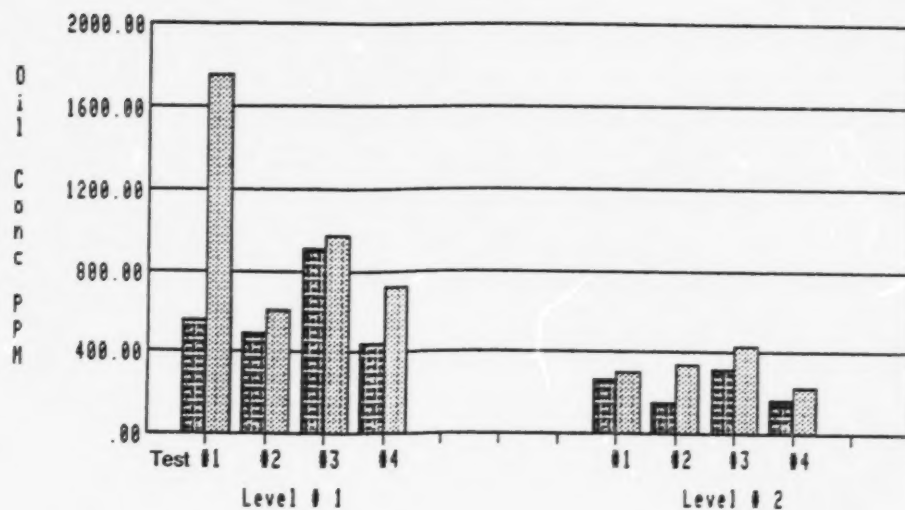
The objective of this study was to develop an efficient, ship-based, oil spill dispersing system using a high-pressure water jet mixing concept. Despite the current emphasis on using aircraft to apply dispersants onto offshore oil spills, ship-based dispersing operations remain suitable for small, near shore spills or for the treatment of relatively small, continuous oil discharges from a damaged tanker or oil-well blowout. One major advantage they hold over aerial systems is the ability to add additional mixing energy to the interface of oil and sea to improve the effectiveness of the chemical being applied. Another is greater control over the dispersant spray pattern. Work carried out in 1983 to develop better ship-based dispersing systems identified a simple, yet promising, mixing concept using high-pressure, relatively low-volume water jets to assist the dispersion process (S.L. Ross Environmental Research Ltd. 1983).

The ultimate goal of this study was to identify the effects of mixing jet pressure, mixing jet flow rate, jet stand-off distance, and cart speed on the dispersion process to better evaluate the potential of the high pressure water jet concept.

Test Methodology and Conditions

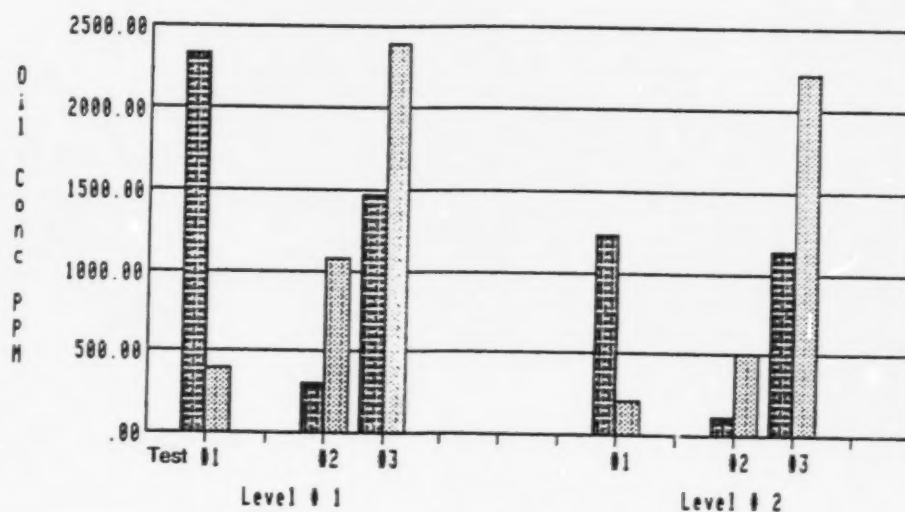
A total of 65 large-scale laboratory tests simulating ship speeds from 1 to 3 m/s were conducted to study the effects of nozzle pressure, nozzle flow rate, and nozzle-to-water separation on the ability of high-pressure water jets to disperse oil slicks. The general procedure used for each test is summarized below.

- Step 1: Spray boom and nozzles were chosen to apply a dispersant dosage of 1:l00.
- Step 2: The test tank was filled 1-m deep, with cold salt water (32 ppt).
- Step 3: The mixing nozzle providing the desired flow rate at the test pressure was selected and attached to the cart at the test height above the water surface.
- Step 4: Six litres of oil was spread evenly over the water surface and was allowed to equilibrate.
- Step 5: The dispersant pump was started and the spray boom was released to apply the dispersant.
- Step 6: The high-pressure water jet was started.
- Step 7: The driver motor was started, propelling the cart across the sampling area.



2nd Appl.
1st Appl.

FIGURE 3 OIL CONCENTRATION COMPARISON: NO BACKGROUND MIXING



2nd Appl.
1st Appl.

FIGURE 4 OIL CONCENTRATION COMPARISON: WITH MIXING

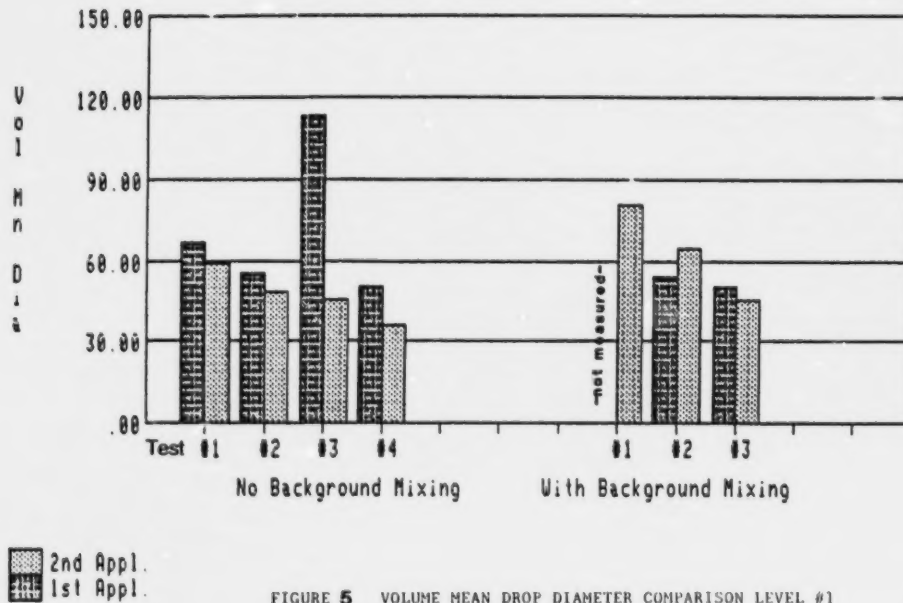


FIGURE 5 VOLUME MEAN DROP DIAMETER COMPARISON LEVEL #1

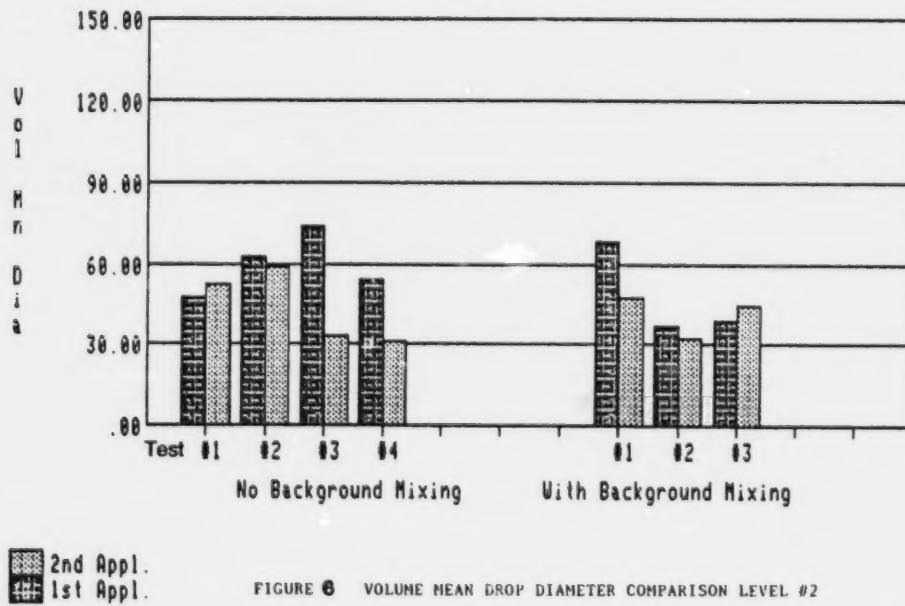


FIGURE 6 VOLUME MEAN DROP DIAMETER COMPARISON LEVEL #2

TABLE I
Summary of oil properties during testing

Test condition	Oil density		Oil viscosity		Oil-water interfacial tension	
	Before ^a	After ^b	Before	After	Before	After
<u>Procedure I: No. Background Mixing</u>						
Test 1	0.85	0.860	9.8	12.8	20.5	5.7
Test 2	0.85	0.863	7.6	9.2	18.2	11.6
Test 3	0.85	0.863	9.0	9.3	22.5	3.1
Test 4	0.85	0.863	8.2	9.5	18.4	4.8
<u>Procedure II: With Background Mixing</u>						
Test 1	0.86	0.857	10.2	11.3	9.2	1.4
Test 2	0.84	0.857	7.7	8.6	15.0	1.6
Test 3	0.85	N/A	8.2	N/A	13.4	N/A

N/A - not available: samples not taken.

- a "Before" refers to the property before the 1st application of dispersant/mixing energy.
 b "After" refers to the property after the 1st application of dispersant/mixing energy and before the 2nd application.

- Step 8: At the first sighting of oil in the photographic cells, drop-size photography and water sampling were started simultaneously. One to three photographs and eight to ten water samples were taken at each depth to "catch" the peak concentration of dispersed oil.
- Step 9: Oil was extracted from the samples with toluene. The volume of each sample was recorded and the extraction was labelled and stored. The oil content of the extractions was later established by a UV spectrophotometer.

Conditions which were kept constant during the testing are listed below.

* Oil type	Alberta Sweet Mixed Blend Crude Oil
* Oil thickness	0.5 mm
* Oil age	Fresh
* Dispersant type	COREXIT 9527
* Dispersant dosage	1:100
* Dispersant drop size	925 μ m volume median diameter
* Water salinity	32 ppt
* Water temperature	15 to 20°C
* Air temperature	20 to 25°C
* Nozzle type	flat fan (20° or 30° divergence)

The following parameters were varied during the testing to evaluate the effects of each on dispersion efficiency. Because of a limited nozzle selection and pump capacity not all combinations of pressure and flow rate were matched.

* Jet stand-off distance	0.6 and 1.5 m
* Jet pressures	7 000, 28 000, and 50 000 kPa
* Jet flow rates	15, 30, and 45 L/min
* Cart speeds	1, 2, and 3 m/sec

Test Results

The complete results of the testing program are summarized in Figures 7 to 18. Figures 7 to 9 illustrate the effect of nozzle flow rate on dispersion efficiency for the small stand-off distance (Figures 10 to 12 for the large stand-off distance). Figures 13 to 15 show the dependence of dispersion efficiency on nozzle pressure for the 0.6 m jet stand-off (Figures 16 to 18 for the 1.5m stand-off distance). A complete discussion of these figures is provided in the final report. The following is a brief discussion of the major findings of the study.

Dispersion efficiency at slow operating speeds (1 m/s) and small nozzle stand-off distances (0.6 m) was found to be very good. Nozzle pressure had little effect on dispersion efficiency at these conditions. Higher pressures were beneficial at higher operating speeds but pressures up to 80 000 kPa (12 000 psi) were needed to duplicate the low speed results.

Increased nozzle flow rates greatly improved the dispersion efficiency at the lower operating speeds for all pressures. Dispersion efficiencies up to 80% were measured with flow rates of 45 L/min. Data extrapolation indicates that 100% dispersion could be achieved in the laboratory with a nozzle flow rate of 50 - 60 L/min at even the lowest pressure tested.

Large nozzle stand-off distances were found to generate a reduced oil dispersion efficiency: a placement of 1.5 m was from two - seven times less effective than the smaller separation (0.6 m). Increased nozzle flow rates, or pressures, or both can overcome this reduced efficiency to some extent.

As it is difficult to translate the laboratory test results to those which would be achieved under typical offshore or nearshore conditions, for comparison purposes laboratory experiments were also conducted with the well-known Warren Spring Laboratory (WSL) breaker board system.

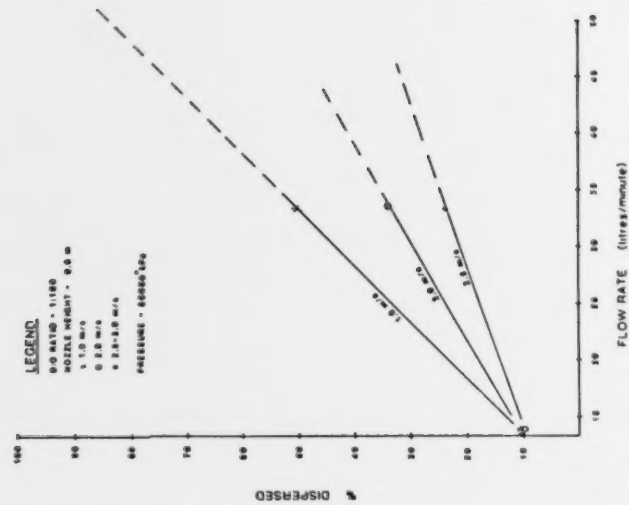


FIGURE 9 Dispersion Efficiency vs Nozzle Flow Rate
(50000 kPa and 0.5 m standoff)

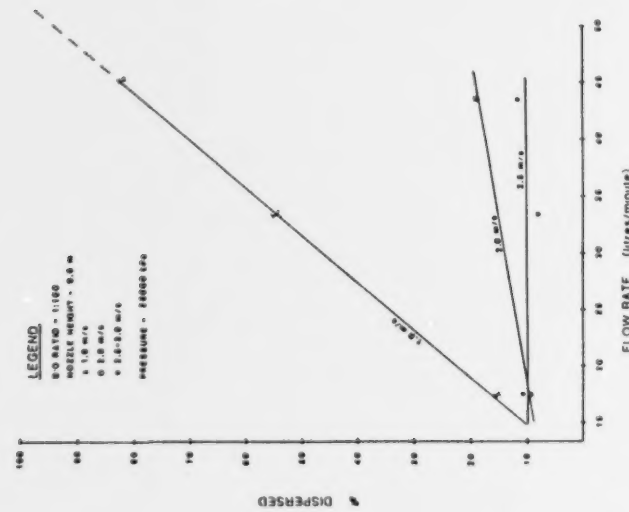


FIGURE 8 Dispersion Efficiency vs Nozzle Flow Rate
(28000 kPa and 0.5 m standoff)

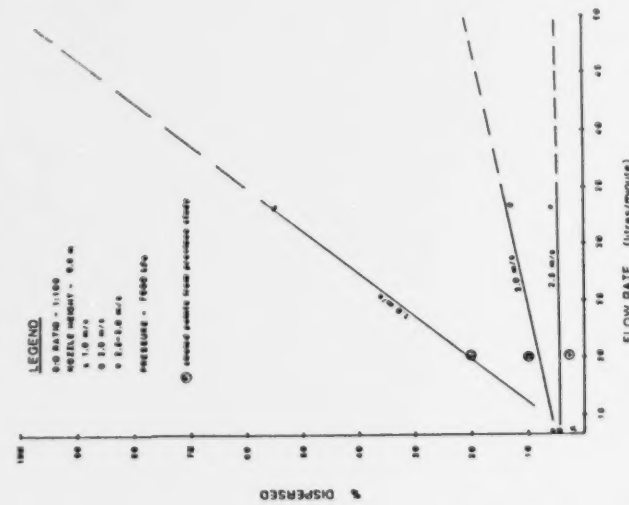


FIGURE 7 Dispersion Efficiency vs Nozzle Flow Rate
(7000 kPa and 0.5 m standoff)

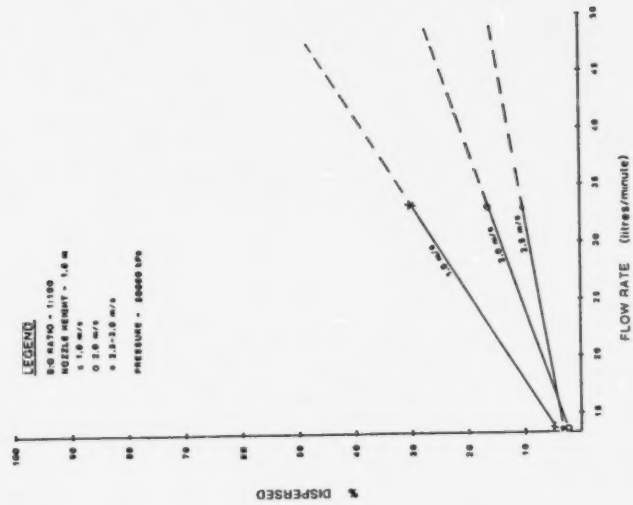


FIGURE 12 Dispersion Efficiency vs Nozzle Flow Rate
(50000 kPa and 1.5 m standoff)

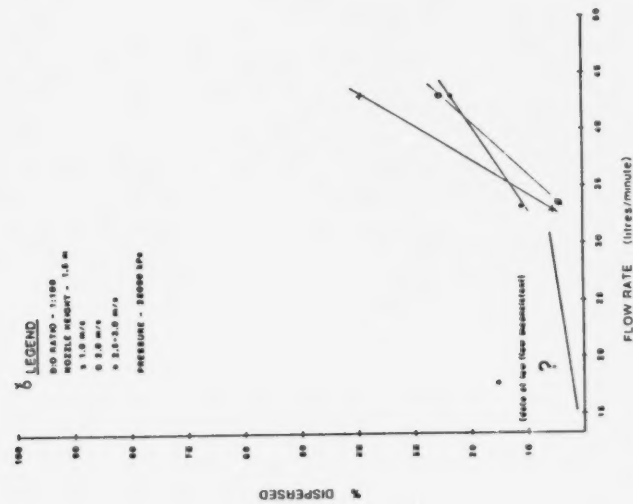


FIGURE 11 Dispersion Efficiency vs Nozzle Flow Rate
(28000 kPa and 1.5 m standoff)

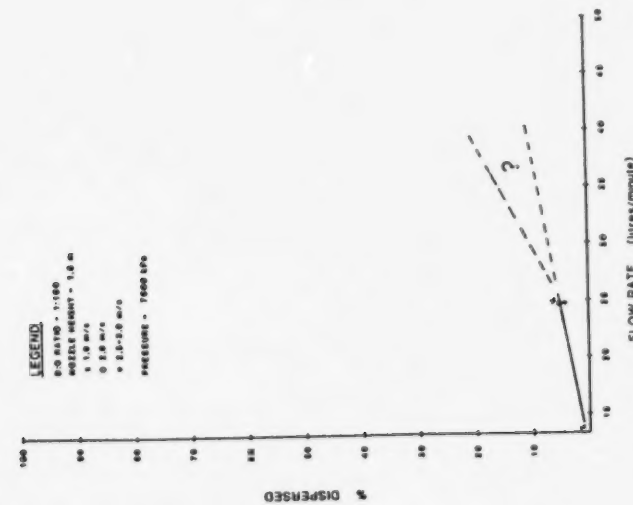


FIGURE 10 Dispersion Efficiency vs Nozzle Flow Rate
(7000 kPa and 1.5 m standoff)

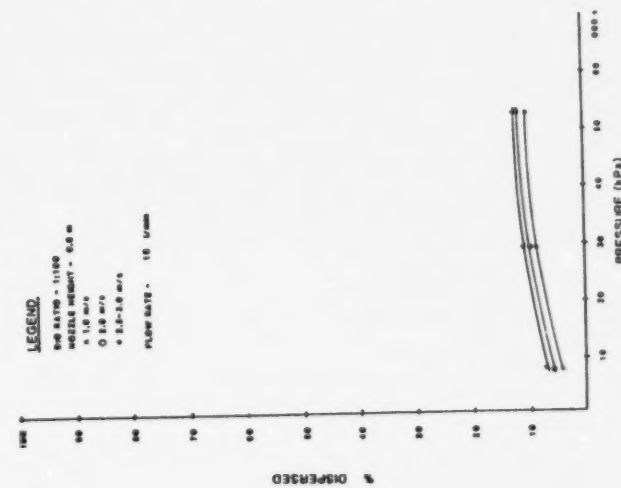


FIGURE 13 Dispersion Efficiency vs Nozzle Pressure
 (15 l/min and 0.6 m standoff)

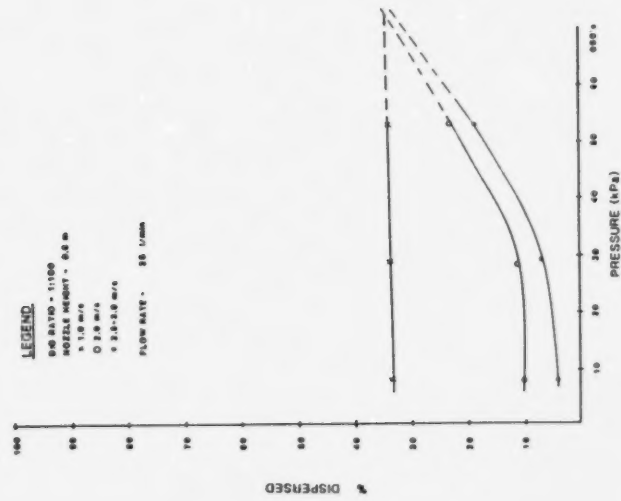


FIGURE 14 Dispersion Efficiency vs Nozzle Pressure
 (25 l/min and 0.6 m standoff)

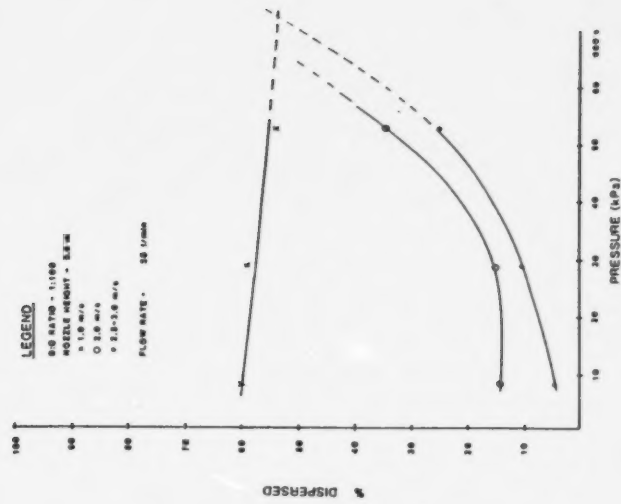


FIGURE 15 Dispersion Efficiency vs Nozzle Pressure
 (35 l/min and 0.6 m standoff)

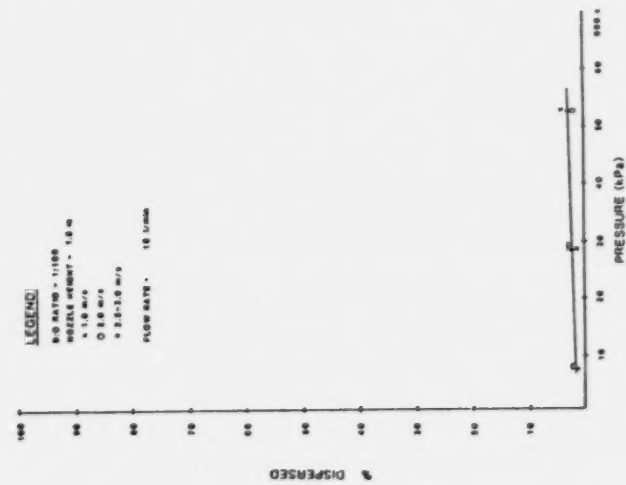


FIGURE 16 Dispersion Efficiency vs Nozzle Pressure
(15 l/min and 1.5 m standoff)

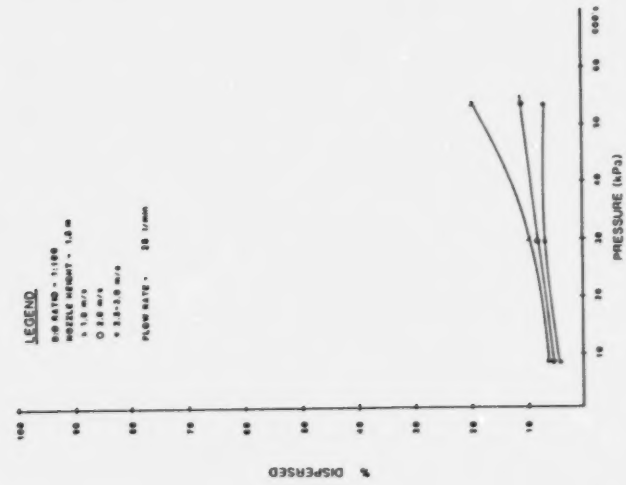


FIGURE 17 Dispersion Efficiency vs Nozzle Pressure
(25 l/min and 1.5 m standoff)

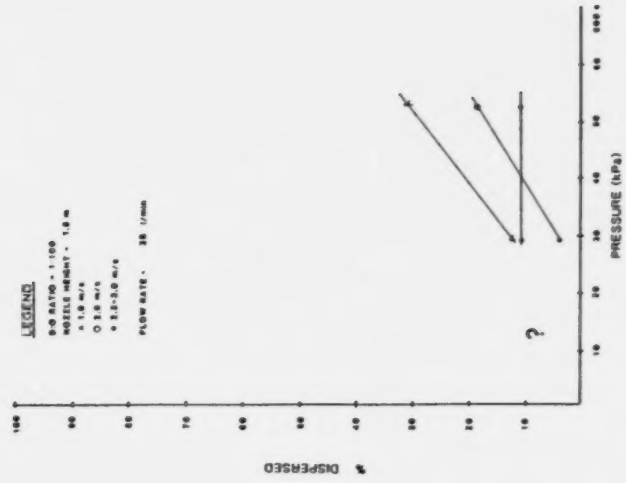


FIGURE 18 Dispersion Efficiency vs Nozzle Pressure
(35 l/min and 1.5 m standoff)

As shown in Figure 19 the high-pressure water system was found to be much more effective than the WSL breaker boards at the slow speeds. At operating speeds of 2.5 - 3.0 m/s, the water jet system becomes slightly less efficient than the breaker boards but neither system, in any case, appears to be efficient at these high speeds.

Based on the test results, specifications for a practical high-pressure water jet system have been suggested. The system would operate with a nozzle pressure of 7000 kPa, a flow rate of 55 L/min per nozzle, and nozzles positioned about 0.6 m from the water surface.

Recommendations for further development of the mixing system include the construction of a nearshore duty prototype system with the above-noted specifications, the testing of the system under typical nearshore conditions to evaluate the system's durability, handling and efficiency, and finally the development of an offshore system if the results of the prototype testing are encouraging.

Study #3: Meso-Scale Laboratory Dispersant Effectiveness Testing

Ever since chemical dispersants were developed to treat offshore oil spills, there have been ongoing attempts to develop a simple laboratory test to predict the effectiveness of these chemicals under actual field conditions. There are now several dispersant effectiveness tests available but it has been demonstrated by several reviewers that all of these are poor simulators of the chemical dispersion process in field situations (Wells and Harris 1979, Nichols and Parker 1985, Delvigne 1982, Lichtenthaler and Daling 1983, and Fingas 1985). Reasons for inconsistent results between effectiveness tests, some of the omissions in testing procedures and the key design parameters for dispersant effectiveness testing have all been discussed to some extent by these reviewers.

The problem with most tests is that, in trying to keep them simple, inexpensive and short, they have sacrificed several key processes which are known to be crucial in determining dispersant effectiveness in the field. For example, none properly simulates oceanic mixing.

The purpose of this project has been to develop a larger-scale test which incorporates all processes that are believed to be important in determining effectiveness in field applications. It is hoped that the result will be a more accurate simulator of the offshore dispersion process. This will permit a realistic evaluation of dispersant effectiveness prior to expensive offshore tests; ideally, it may actually obviate the need for such tests.

Key Factors to Consider in the Laboratory Simulation of the Chemical Dispersion Process

There are four main processes or events which must be modelled in a laboratory test to simulate the chemical dispersion of the oil. These are:

- i) The oil is spilled and spreads and ages prior to the application of dispersant.
- ii) The dispersant is applied in a spray form to the surface of the oil slick and interacts/mixes with the oil and water system.
- iii) Natural ocean wind and wave mixing energy (or artificial mixing by breaker boards, high pressure water, propellor wash etc.) breaks the slick into an oil-in-water dispersion of a particular drop-size distribution.
- iv) Entrainment of the smaller droplets into the water column takes place and larger drops eventually re-surface and re-coalesce if the ocean's turbulence is insufficient to retain the drops within the water mass.

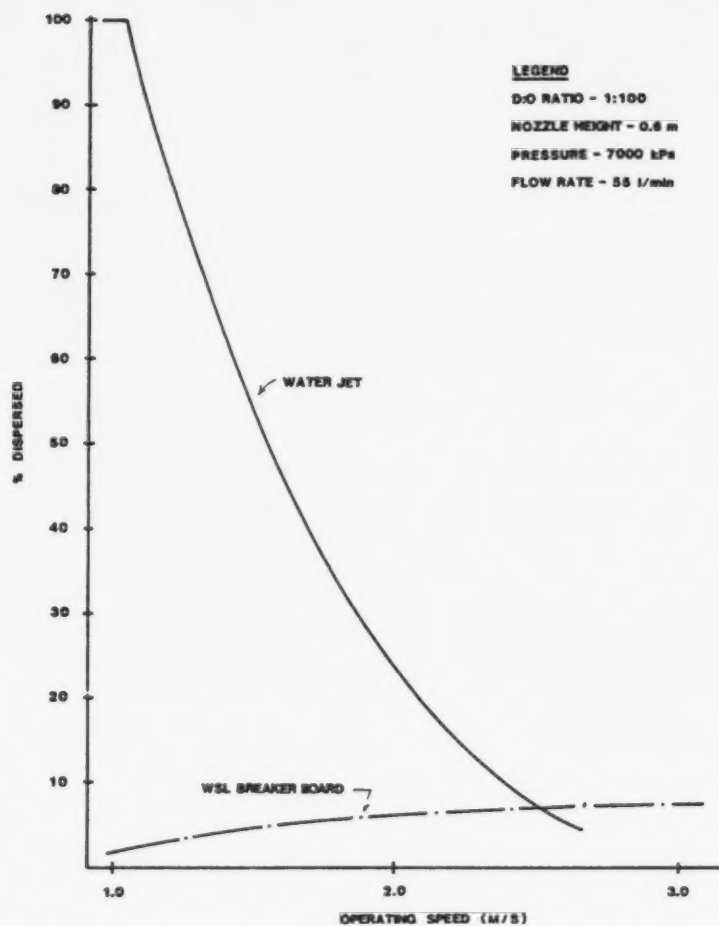


FIGURE 19 Comparison of Proposed Practical Water Jet System with WSL Breaker Board

A series of preliminary effectiveness tests have been completed in the test tank discussed earlier in this paper. These larger scale tests have enabled us to simulate and control major dispersion processes in a much more realistic manner than can be achieved in small bench scale tests.

Test Methodology and Conditions

The tests were conducted as follows:

- Step 1: The tank was filled with cold salt water (10°C and 32 ppt).
- Step 2: The wave generator and wind tunnel were activated to provide the desired mixing energy for the tests. (After selecting the desired wave height the wind is adjusted to hold the oil in the centre of the test tank.)
- Step 3: Oil was placed in the centre of the tank and allowed to equilibrate for 15 minutes.
- Step 4: Background oil concentrations and dispersed oil drop size measurements, oil slick thickness, and oil-water interfacial tensions were taken prior to dispersant application.
- Step 5: Dispersant was applied to the slick from a spray boom towed above the tank surface inside the wind tunnel.
- Step 6: Samples were taken for dispersed oil concentrations and drop sizes, oil slick thickness (where applicable), oil-water interfacial tension measurements and dispersant concentration in both oil and water immediately after the application of dispersant, and 15, 30 and 60 minutes after application.
- Step 7: The samples taken during the testing were either analysed immediately or prepared for future analysis.
- Step 8: The tank was drained and cleaned with a high pressure washer to prepare it for the next test.

A total of 16 of these large scale tests were completed for this study. Conditions left constant during the testing are listed below.

* Water temperature	10°C
* Air temperature	20°C
* Water salinity	32 ppt
* Dispersant Application Dosage	1:20
* Dispersant Application Nozzles	Spraying Systems Co. 1501 and 1502 flat fan.
* Dispersant Application Pressure	100 psi

The parameters varied in the testing were as follows.

* 2 Dispersant types	Corexit 9527 and Enersperse 700
* 2 Oil thicknesses	1.0 mm and 0.5 mm
* 2 Oil types	fresh Alberta Sweet Mixed Blend and weathered ASMB (1000 cst @ 10°C)
* 2 Mixing energies	15 cm and 20 cm wave heights

At the time of preparation of this paper the laboratory testing had been completed but the data not yet analysed. Results will be presented during the AMOP seminar.

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IN-TANK DISPERSANT MIXING STUDY

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ABSTRACT

Scale model experiments of mixing in rectangular tanks by line bubble plumes are described with the object being to predict mixing of dispersant into crude oil in full sized oil tanker compartments. The gas bubble plume was created by air exiting from a line source at the bottom of tanks filled with water. Flouroscein dye was used in the tanks to trace the mixing. From samples of tank fluid during the mixing, the average dye concentration variation was calculated and used to describe the amount of mixing left to be completed.

Through dimensional analysis it was determined that the Froude number was the most important dimensionless group and the independent variables of the system were defined. The resulting change in mixing during the experiments as the independent variables were varied was noted. The data was nondimensionalized and plotted in log-log form so that a straight line could be fitted through the points. An exponential relationship between average concentration variation and mixing time was derived. Using the bubble plume, dispersant was mixed into crude oil in the model tank to confirm the results and check the influence of viscosity. Dispersant mixing times in full sized tanks containing crude oil are predicted.

INTRODUCTION

When a stream of gas bubbles is released at the bottom of a tank of fluid, the bubbles and entrained liquid form a rising plume. Such a plume mixes fluids effectively because of the turbulent mixing in the plume region coupled with the induced convection which circulates the fluids through the plume. Here, we report on the mixing induced by gas bubbles released from perforated horizontal pipes in open-top rectangular tanks and the dependence of the mixing on the independent variables of the system. This leads to a fomulation for predicting the mixing in tanks of any size with any gas flow.

The principal motivation for the work was the possibility of rapidly mixing treating agent into the oil in a large ship tank after damage to the tank, but before much of the oil escapes. This can materially reduce pollution damage through use of dispersant, sinking agent or gelling agent as the treating agent; the best choice being dependent on circumstances. Thus we

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consider mixing of an agent released from the same perforated pipe that releases the gas or from a perforated pipe immediately above the gas pipe.

Because of the ship tank application, a gas release pipe was always along the bottom of a side wall. This wall would correspond to the wall along an exterior ship side that could be damaged so as to maximize the treatment of escaping oil. In some of our experiments a second release pipe leg was along an adjacent wall so the release pipe formed an "L", and in some other experiments the second pipe leg was along a mid-line of the tank bottom so the release pipe formed a "T".

Tests were conducted in a cubical tank measuring 1.22 m along each edge at fluid depths of 0.66 m and 1.22 m, and in a rectangular tank with 1.18 x 1.22 m base dimensions at a fluid depth of 2.44 m. Water was used as the mixing media. The approach taken in the experiments was to release a small volume of fluorescent dye quickly and then to measure the dye concentration distribution as a function of time thereafter. The bubble plume was started either just after the dye release or before it (see below).

Recently tests mixing dispersant into crude oil in the 1.22 m tank, using the same overall procedure as the water tests, were arranged by the sponsors of the study, The Environmental Protection Service of Canada. The tests were conducted by Atomic Energy of Canada Limited (hereafter called AECL) since a radioactive tracer was added to the dispersant previous to mixing. AECL staff then determined the amount of dispersant mixed into the oil samples by radioactive assays. This data was analyzed by the same method as the data from the water experiments.

VARIABLES

The average concentration variation of dye or treating agent in the tank fluid is defined in terms of the local concentration, $c(x,y,z)$ of dye by:

$$S = \sqrt{(1/c_m^2) \iiint_V [c(x,y,z) - c_m]^2 dx dy dz} \quad (1)$$

where c_m is the mean concentration. The integral is to be taken over all the fluid. S , c , and c_m can depend on time.

In the experiments, samples to be analyzed were taken at the same time after the start of mixing from N discrete locations. S was approximated by U (the "unmixedness") defined as:

$$U = \sqrt{(1/c_m^2) \sum_{i=1}^N [c_i - c_m]^2 v_i} \quad (2)$$

where c_i is the concentration at the i 'th location and the mean concentration c_m was determined as the concentration after the tank was allowed to mix for a long time. v_i is a volume

associated with the i 'th location such that for tank volume V ,

$$\sum_{i=1}^N v_i = V \quad (3)$$

For example, locations and volume dimensions for the 1.22 m depth are shown in Fig 1. U is the dependent variable that was measured in the experiments.

For a square based tank and a specific gas release geometry, and neglecting the influence of the viscosity and density of the gas because they are so small compared to those of the liquid, there are ten independent dimensional variables. We found that the results of several gas release geometries could be unified in terms of an effective horizontal length of gas release, L_{bp} , so this is considered as an independent variable. The independent variables are listed in Table 1. The seven independent dimensionless groups (variables) that can be formed from these 10 dimensional variables are : h' , F_r , L' , P_r , Re , t' and We . See Table 2 for their formulations.

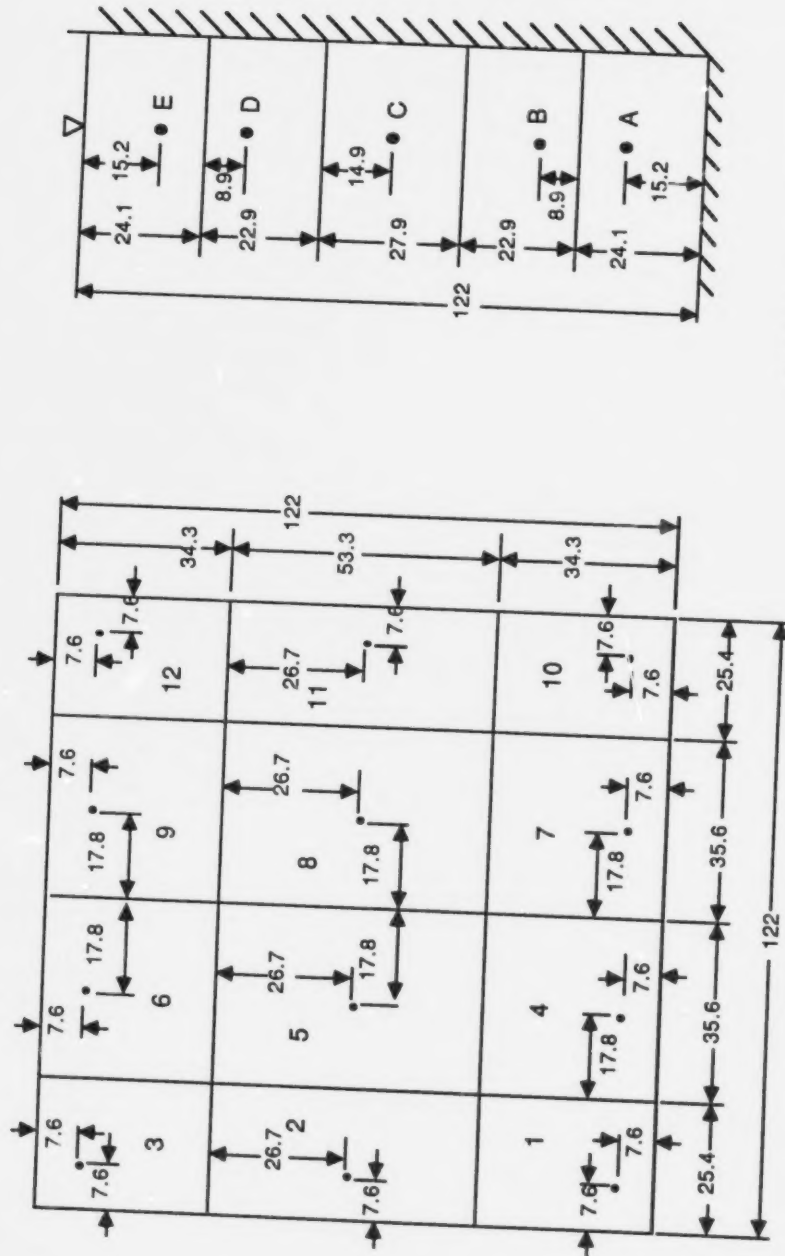
Table 1. Independent Dimensional Variables

h	liquid depth
L	length of width of tank base
g	acceleration of gravity
P	pressure
Q	gas volume flow rate
T	characteristic mixing time
u	fluid kinematic velocity
ρ	fluid mass density
σ	gas-fluid surface tension

Table 2. Formulations of Independent Dimensionless Groups

<u>Group Name</u>	<u>Formula</u>
Height Ratio	$h' = h/L$
Froude Number	$F_r = Q/\sqrt{gL^5}$
Plume Length Ratio	$L' = L_{bp}/L$
Pressure Ratio	$P_r = (P + \rho gh)/P$
Reynolds Number	$Re = u/\sqrt{gL^3}$
Dimensionless Time	$t' = tQ/L^2L_{bp}$
Weber Number	$We = \sigma/\rho gL^2$

Dimensionless variables that were varied significantly in the experiments are: the Dimensionless Time (t'), the Height Ratio



(b) Vertical length of sample volumes for 1.22 m

(a) Horizontal sampling grid

Figure 1. Locations and Dimensions of Sampling Points and Associated Volumes for a Fluid Depth of 1.22 m. Similar arrangements were used for the 0.66 m and 2.44 m depths except they used 4 and 6 heights respectively instead of 5. Note: All dimensions are in centimeters, • sampling point.

(h'), the Froude Number (F_r) and the Plume Length Ratio (L'). Some comment on the other variables is in order.

The Pressure Ratio, P_r , is the ratio of gas volume flux at the top of the tank to the volume flux at the bottom. Under ordinary laboratory conditions it cannot differ significantly from 1.0 unless experiments are done under vacuum which we did not do. Thus we have not determined the influence of P_r on the mixing. In a large ship tank it is about 2. For modest P_r 's our formulations are best applied by using the gas volume flow rate at the tank mid-height. Variations from this would be on the order of 35% for a P_r of 2. As our results will show, 35% variations in gas flow affect U by just a few percent. On the other hand, our results cannot be applied to conditions where the P_r is very large.

The principal influences of the Reynolds number are on the wall boundary layers and on the size of the turbulence microscale. Details of the wall boundary layers are not important in the bubble plume mixing flow. Although the microscale size influences the mixing at very small scales, this is not detected in our experiments in which fluid elements larger than the microscale are sampled for analysis. Therefore, we are not considering the influence of the Reynolds number here.

The Weber number influences the gas bubble diameters which are proportional to $\sigma^{1/2}$ (see Hu & Kinter, Ref. 3 and Milgram, Ref. 2). To determine the influence of this to the extent practical in our laboratory, we did two experiments (Godon, Ref. 1) that were identical except that one had a surfactant in the water which reduced the surface tension by a factor of 2. No significant differences were observed in results of U vs t so we will not consider the influence of the Weber Number here.

PART 1: WATER AND DYE EXPERIMENTS

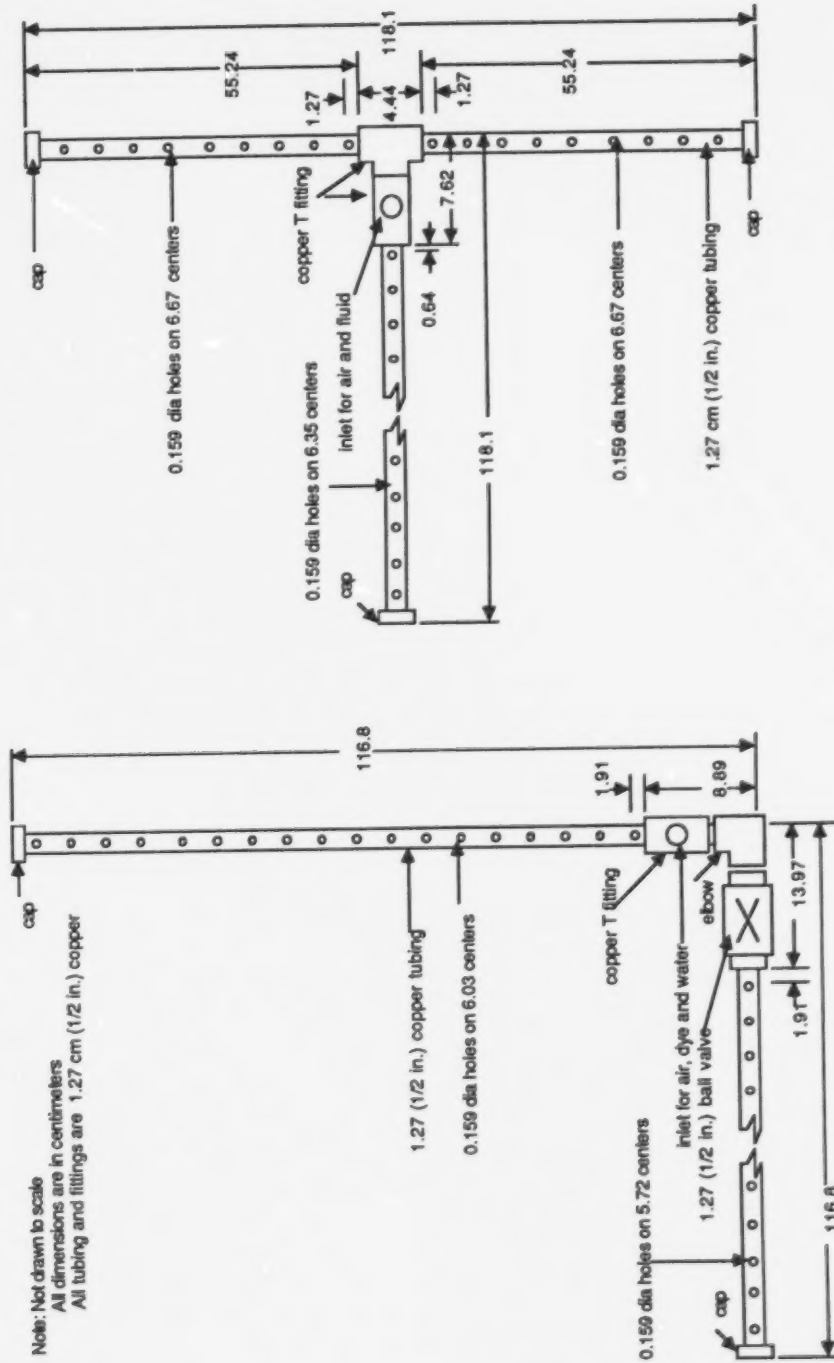
Apparatus and Experimental Procedures

Tap water was used for tank fluid and its temperature was between 15 and 20 C. The fluid to be mixed was tap water containing dissolved fluorescein dye. The fluorescein concentration in each sample of tank fluid taken was determined with a Model A-4 Farrand Fluorometer.

Air escaping through holes in a 12.7 mm ID perforated pipe at the bottom of the tank generated the bubble plume. Tests were done at air flows of 0.32, 0.48, 0.6, 1.1 and 2.0 L/s, referenced to standard conditions. Three different pipe configurations were tested:

- 1) A 1.17 m long straight pipe along one bottom edge,
- 2) A 1.17 x 1.17 m "L" configuration with a pipe along each of two adjacent edges,
- 3) A 1.18 x 1.18 m "T" configuration on the bottom.

Each of the "pipe legs" contained 18 gas release holes of 1.59 mm ID. The pipe configurations are shown in Fig.2. A valve in the "L" configuration permitted it to be used for the single straight pipe tests as well.



(a) Straight Pipe (valve closed) and "L" (valve open)

(b) "T" Pipe

Figure 2. The Gas Distribution Pipes

For some of the tests, the dye was pumped out of the same pipe as was used for the gas. In other tests involving gas pipe configuration (1) (straight pipe), the dye was pumped out of a 1.17 m long straight pipe containing 16 3.18 mm diameter holes and located above the gas pipe at the mid-depth of the fluid.

Samples of the tank fluid were taken with twelve identical small gear pumps with individual inlet and outlet tubes as shown schematically in Fig 3. Each sample pump delivered 18 ml/s and uncollected fluid was returned to the tank. To minimize mixing by the sampling pumps the volume moved by all 12 pumps in an experimental run was limited to 3% of the tank volume. Twelve samples were simultaneously taken at prescribed times with the twelve inlets located at the horizontal grid points shown in Fig 1. Samples were obtained at all the depths by moving the inlets to a different horizontal plane and repeating the experiment.

Fig. 4 shows a general schematic diagram of the experimental arrangement. Three different experimental procedures were used which are now explained.

Procedure #1 - Used with initial tests of straight plume pipe.

The same perforated pipe was used to introduce the dye and the air. First, two samples were taken to determine the background (relative zero) level of dye concentration. The dye pump was started and dye was pumped for 20 seconds. Without stopping the dye pump, its inlet flow was switched from dye to water which was pumped for 15 seconds to flush any remaining dye out of the pipe. At the end of the 15 second water pumping period, the dye pump was stopped, the timer was started and the air flow was started. The sampling pumps were started with their outlet flows going back into the tank. At a predetermined time, typically 30 seconds, a rack of 4 mL glass cuvettes was moved under the sample streams. They filled in about 0.25 sec. and the rack was withdrawn. At predetermined regular time intervals additional racks of cuvettes were filled.

After the desired sets of samples were obtained, the tank was allowed to mix under the plume action for 10 to 15 minutes. Then four samples were taken to determine the average dye concentration.

Initial experiments showed that all measurements at the 0.66 m depth and those at the 1.22m depth taken less than 60 seconds after the start of a run and with a low gas flow (0.32 L/s) were influenced not only by the gas plume mixing, but also by the initial mixing caused by the method of dye introduction. These data were eliminated from further consideration. Procedure #2 was found to cause only about half as much pre-mixing as Procedure #1.

Procedure #2 - Used with later tests of straight plume pipe.

Separate distribution pipes were used for air and dye with the dye pipe at the mid-depth of the fluid. Two background-level samples were taken. The gas flow was started and about 30 seconds later

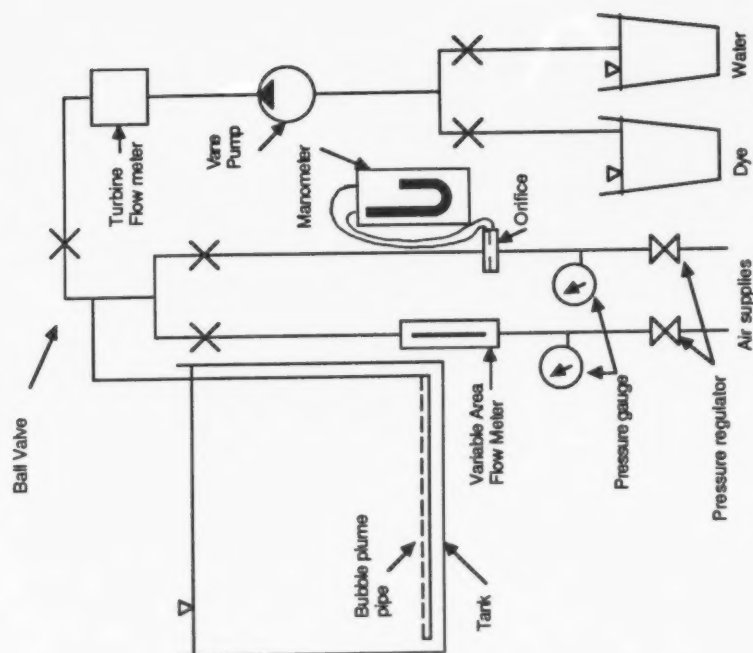


Figure 4. General Experimental Arrangement
The orifice meter was used for gas flows greater than 1 L/s and the variable area flow meter was used for all lower gas flows. When a separate pipe was used to introduce the dye, the dye flow was attached to that pipe instead of the gas flow pipe as shown here.

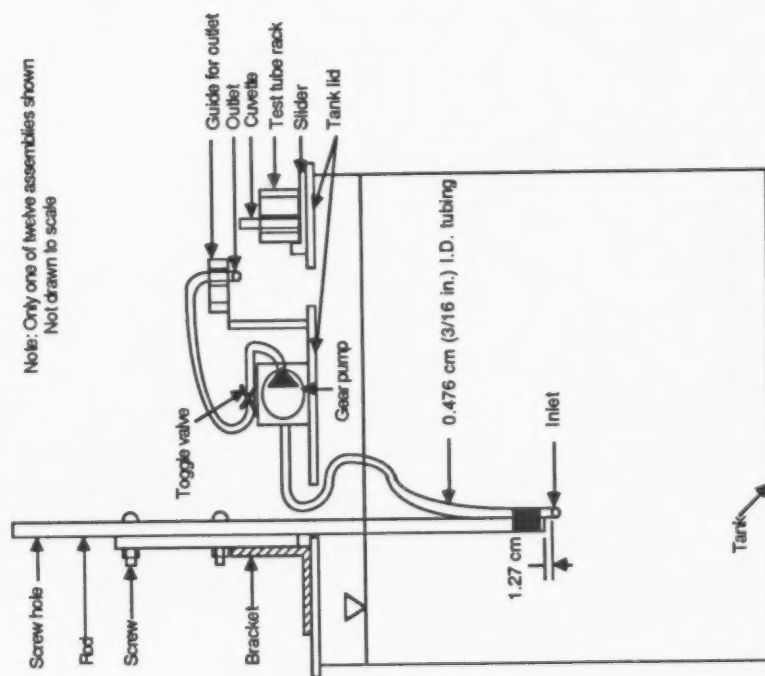


Figure 3. Sampling Pump and Tubing Arrangement

(to allow for establishment of the plume) the dye flow was started. Five seconds later the dye pump inlet was switched from dye to water which was pumped for 15 seconds after which the pump was stopped and its valves were closed. The sampling pumps were started with their outlet flows returning to the tank. The timer for sample collection was started midway through the dye introduction.

Fig 5 shows comparative measurements using procedures #1 and #2 with straight plume distribution pipes containing the procedure #1 data that was eliminated from consideration. The retained data, not all of which is contained in Fig.5, has difference in U on the order of 0.06 between the two procedures, but without a clear trend. We believe that these are due to both pre-mixing differences and to our ability at making accurate fluorometer measurements which improved during the experimental program.

Procedure #3 - Used with tests of "L" and "T" plume pipes. This was identical with Procedure #2 except here the same distribution pipe was used for gas and dye. Data was taken at a gas flow of 0.48 L/s with a fluid depth of 1.22m. For these conditions with the straight distribution pipe results were little influenced by the choice of the procedure.

Water and Dye Data

The raw data are sets of values of c_1 for specific values of Q , h and t . Each set contained 48, 60 or 72 values for depths of 0.66, 1.22 or 2.44 m respectively.

The reduced data is comprised of all values of U vs t except for the aforementioned part of the procedure #1 data that was influenced by initial pre-mixing. Fig 6 shows the reduced data for a straight plume distribution pipe and fluid depths of 1.22 and 2.44 m. For each gas flow the results for the two different depths are very similar.

Fig 7 shows the reduced data for a gas flow of 0.32 L/s for fluid depth of 0.66, 1.22 and 2.44m. It should be noted that the 0.66 m depth mixes faster. For much of the time history, the 0.66m depth has values of U that are about 0.15 less than that of the other depths. At a slightly higher flow rate of 0.48 L/s this trend is much less noticeable with only one data point on the 0.66 m curve disagreeing with the curves of the two other depths.

We have identified three contributing causes for the apparent faster mixing at low gas flow for small fluid depth. One is the premixing due to introduction of the dye which is more apparent when the total tank volume is small. Since increased gas flow increases the mixing rate, a pre-mixing error will be more apparent at low gas flow. Secondly, the cross-sectional shape of the bubble plume has an initial width near the bottom followed by a linear increase in width with height. For the low depth case, the ratio of average plume width to fluid height is slightly higher than in the deeper fluid cases. Thirdly, the ratio of bubble diameter to average plume width is largest for the lowest

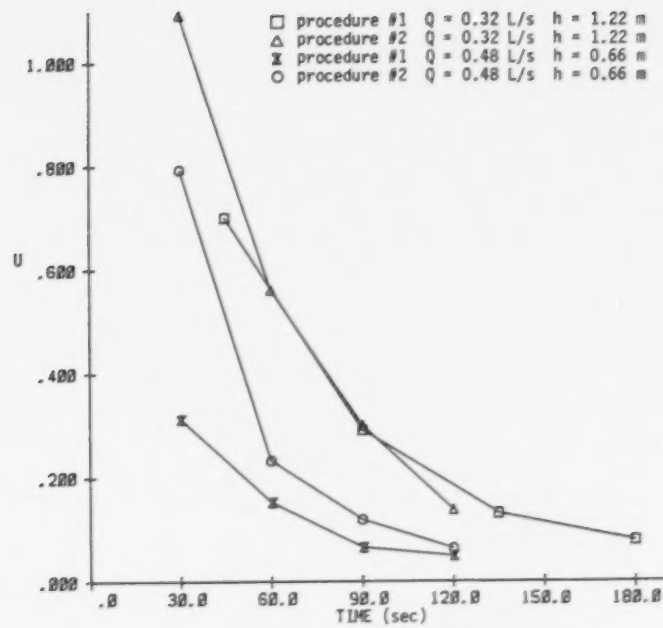


FIGURE 5

SOME COMPARATIVE MEASUREMENTS FOR PROCEDURES 1 & 2

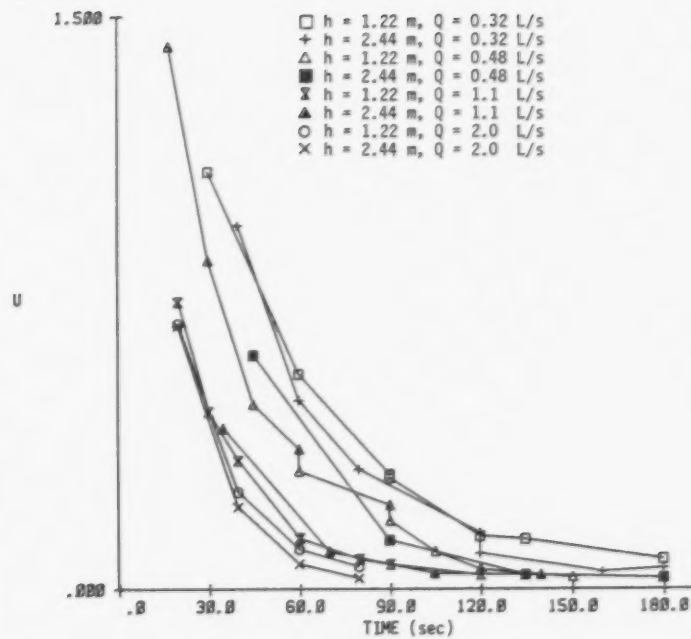


FIGURE 6

REDUCED DATA (U vs t) FOR THE STRAIGHT DISTRIBUTION PIPE AND FLUID DEPTHS OF 1.22 AND 2.44 METERS.

Note that as gas flow increases the mixing increases.

height. The mixing due to individual bubbles at the outer part of the plume may be most influential for this condition.

Fig 8 shows reduced data at a fluid depth of 1.22 m and a gas flow of 0.48 L/s for all three plume distribution pipe configurations: straight pipe, "L" and "T". The "L" mixes considerably faster than the straight pipe and the "T" mixes considerably faster than the "L". Data for the straight distribution pipe with a gas flow of 1.1 L/s is included in Fig 8. This shows that the "T" configuration at a gas flow of 0.48 L/s mixes as fast as the straight pipe at a gas flow of 1.1 L/s.

Data Accuracy

Assessing the accuracy of the measured data, c_i and t is straightforward. The sampling times are accurate to within 2 seconds. Repeated fluorometer measurements yielded concentrations that never varied by more than 4% of the measured value so this error bound is valid with at least 95% confidence. 48 to 72 values of c were averaged to determine U so values of U , as defined by eq(2) were determined with errors of less than 1% of their values with high confidence.

Since the measurement process determines values of U with high accuracy, the more important issue is how well U approximates the tank mixing. Three different approaches were used to determine the uncertainty of U : comparing results from experiments at the same gas flow rate and depth; comparing mean concentration calculated from the samples to the concentration measured after the tank had been completely mixed; and approximating the uncertainty based on theoretical statistics. On the basis of these calculations the standard deviation of U is about 2% leading to a 7.6% uncertainty in U for 95% confidence.

DATA ANALYSIS

The goal of the data analysis is to determine how the average concentration variation, U , depends on the dimensionless variables t' and F_r . To find the most influential dimensionless variable we consider a new dimensionless independent variable t'' defined by:

$$t'' = (t')^a (F_r)^b (h')^e (L')^f \quad (4)$$

For a straight distribution pipe ($L_{bp} = L$), the best values of e and f were very nearly zero. Then for all data points we seek the values of a and b which most closely "collapse" the points to a single line on a plot of U vs t'' . For the straight distribution pipe data the best values of a and b were found to be 1 and $-8/15$ respectively. Thus, equation (4) can be simplified as:

$$t'' = t' F_r^{-8/15} \quad (5)$$

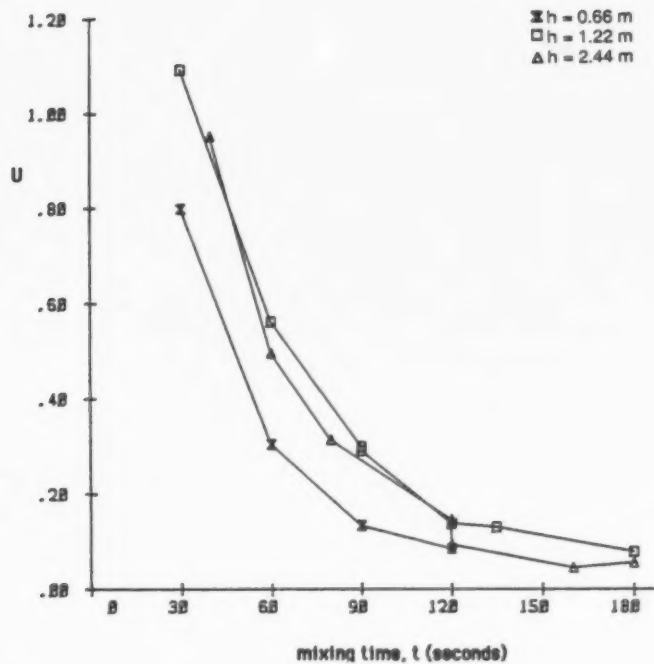


FIGURE 7

REDUCED DATA FOR THE STRAIGHT DISTRIBUTION PIPE AND A GAS FLOW OF 0.32 LITERS/SECOND

Note that the 0.66m depth case appears to mix considerably faster than the others.

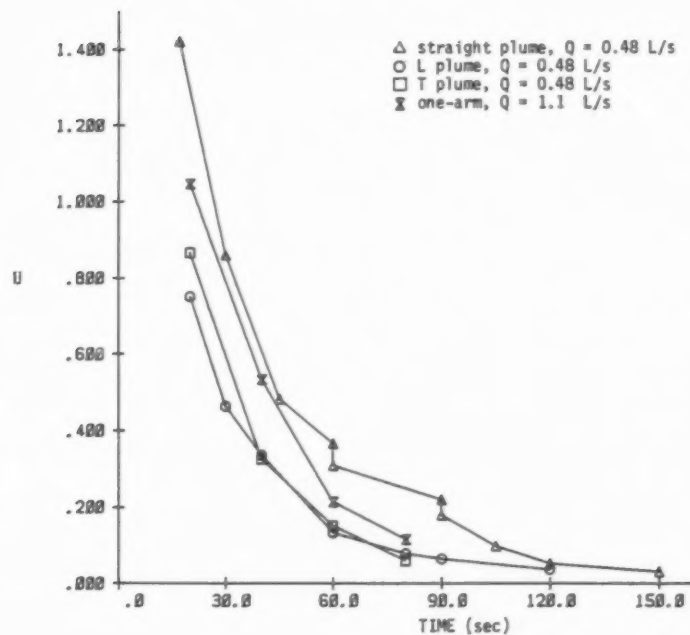


FIGURE 8

REDUCED DATA FOR A FLUID DEPTH OF 1.22 m AND A GAS FLOW OF 0.48 LITERS/SECOND FOR THREE DISTRIBUTIONS PIPE CONFIGURATIONS.

Data for the straight pipe at a gas flow of 1.1 L/s is included for comparison.

Fig 9 is a log-log graph of U vs t'' for the straight pipe data. To understand the meaning of t'' we express it as:

$$t'' = t/T$$

where the characteristic mixing time T can be interpreted in terms of two "physical" times. One is the time it would take for the gas flow to fill a volume $L^2 L_{bp}$. We call this T_1 .

$$T_1 = L^2 L_{bp} / Q \quad (6)$$

The second physical time T_1 is proportional to the time it would take to circulate all the tank fluid through the bubble plume once. The cross-sectional shape of the plume is shown in Fig 10 where k is the slope of plume width vs height, typically about 0.1. The flow in the plume is generally upward except very near the surface where it turns horizontal. The characteristic vertical liquid velocity, V_f , just before it turns horizontal can be found by equating the vertical momentum flux in the plume to the buoyancy and by neglecting the "slip speed" of the gas since it is smaller than V_f .

$$V_f = (Qg/L_{bp})^{1/3} \quad (7)$$

Since the liquid volume flux out of the plume is $khV_f L_{bp}$, the time T_2 for the tank fluid to pass through the plume once is:

$$T_2 = (L^2/L_{bp}) / (Qg/L_{bp})^{1/3} \quad (8)$$

With these forms for T_1 and T_2 the data collapses best when T is expressed as:

$$T = T_1^{0.2} T_2^{0.8} \quad (9)$$

To obtain an approximating analytical relationship between U and t'' the data is plotted in log-log form in Fig 9 where it is shown that the data is well approximated by:

$$U = \begin{cases} 0.98 (t'')^{-1.21} & , t'' < 2.65 \\ 3.63 (t'')^{-2.57} & , t'' > 2.65 \end{cases} \quad (10)$$

How well are the "L" plume and "T" plume distribution pipe data approximated by eq (10)? In seeking to answer this we note that for the "L" configuration $L_{bp} = 2L$. In determining L_{bp} for the "T" configuration the derivation of T_2 is examined. In this regard, since the plume width above the center leg of the "T" is twice the width of the plume above a pipe along a wall, the correct value to use for L_{bp} in the case of the "T" pipe is $3L$. Using this, with T defined by eq (9) and T_2 defined by eq (8) the results for the "L"

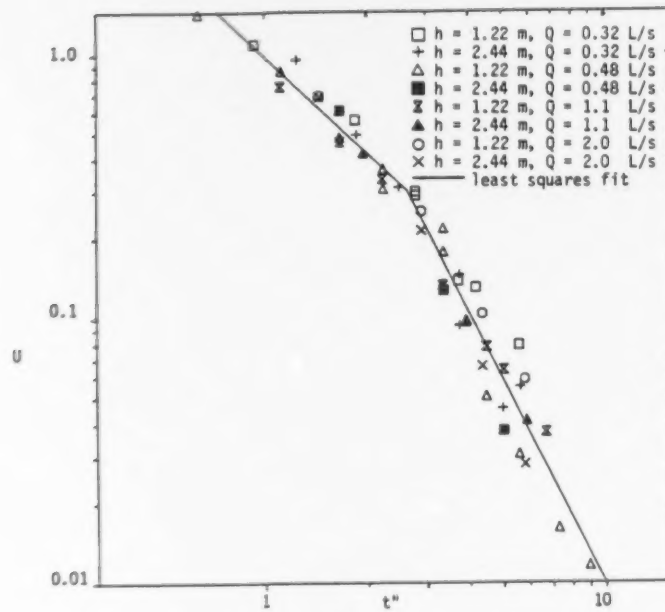
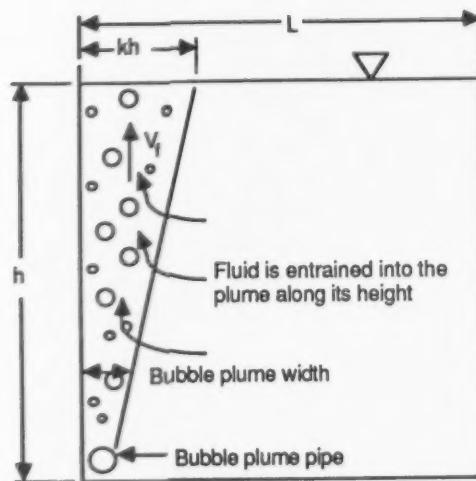


FIGURE 9

LOG-LOG PLOT OF U vs t'' 

Note: not drawn to scale

Figure 10. Schematic Bubble Plume Crosssection

and "T" configurations are shown in Fig 11. Eq (10) is a good approximation to the data.

PART 2: OIL AND DISPERSANT EXPERIMENTS

Apparatus and Experimental Procedure

The tank and plume generation apparatus as described earlier were used. The tank was filled to a depth of 1.22 m with sweet Alberta crude oil. Plume gas and dispersant were introduced by procedure 2 with the straight distribution pipes. The dispersant was introduced above the gas at the mid-depth. We hasten to point out that this arrangement is not required to make the mixing procedure work in a ship. Any procedure which introduces the treating agent into the bubble plume will work. It is anticipated that the gas and treating agent would come from the same pipe in a ship tank.

To minimize the danger from hydrocarbon fumes the tests with oil were conducted out of doors and nitrogen was used as the plume gas. The outside temperature varied from 0 to +13 degrees C. The nitrogen flow of 0.6 L/s was started first. After the plume was established, the radioactive dispersant was introduced over a period of 10 seconds by opening a valve from a pressurized dispersant tank. Mixing time was "started" 5 seconds after the valve was opened. The same procedure in sample taking as previously described was observed with a separate treating agent introduction for each height.

Two different fillings of the tank with oil were used. For each of these, there was no dispersant in the oil before the tests.

For the first filling of the tank with oil, a gravity-feed sampling system was used. It took 40 seconds to collect the sample size required by AECL, so the gravity-fed samples are representative of the mean concentration at each sampling location, but they are not at all representative of the unsteady concentration fluctuations. The reason is that over the relative long time of 40 seconds, many "regions" of fluid are swept past the entrance of a sampling tube by the flow.

For the second test, to minimize the effect of averaging due to sampling time, the sampling pumps from the water tests were used and the sampling size was reduced after consultation with AECL. With this arrangement samples were acquired over 3 seconds. Although this is an improvement, the samples were still influenced by spatial averaging since the typical flow speed in the tank is 10 to 20 cm/sec. For this filling there was insufficient radioactive tracer to do the experiment at all five sampling heights, so tests were done at just three heights: A, C, and E (see Fig 1).

To obtain limited data without significant averaging due to sampling time, grab samples were taken near the top of the tank during tests with the second filling of oil.

Analysis of the Oil Experiments

The AECL staff determined radioactivity levels of all samples and reduced these measurements to percentages of fully mixed concentration. For the first tank filling (5-height data) with 60 points, we processed the data to determine U , exactly as with the tests in water. For the second tank filling (3-height data) with 36 data points we used the same approach, but "assigned" to each point a volume v_i equal to 1/36'th of the tank volume for the computation of U .

For the 3-height data, the mean of each group of twelve samples did not always equal the fully mixed concentration, especially for the second and third sample collection times at height E, and the results seemed to have a bias towards high concentration values. To correct this, U was calculated by using the mean concentration of each group rather than the fully mixed concentration.

Fig 12 shows the values of U for both the oil and a water test all at 0.6 L/s. Figure 13 is a log-log plot of U vs t' , for all the straight pipe data in water at a 1.22 m depth and also the 3-height oil data. Equation (10) is also included in the plot.

Discussion of Oil Results

The influence of averaging due to sampling time is apparent in the data. For short mixing times, calculated values of U are smaller in the oil tests than in the water tests where sampled fluid was taken in a fraction of a second. The 5-height data with 40 second sample acquisition shows lower values of U than the 3-height data with samples acquired in 3 seconds.

For large mixing times, the tests with oil show larger values of U than the water tests. However, this does not imply that there is less mixing of treating agent into the oil. A point-by-point study of the data showed that at large mixing times, larger than expected values of U are mostly due to samples that contain considerably more dispersant than the fully mixed concentrations. So most of the samples have at least the fully mixed concentration of dispersant and many samples have even more. This could be the result of the small sample size of 36 compared to 60 samples taken during the water experiments or errors in the radioactivity measurements, but in any case all the samples have a considerable amount of dispersant in them.

Examining the results of the grab samples in Table 3, the same trend can be observed: During the initial part of the experiment the concentration variation of each sample from the fully mixed value decreases rapidly while at larger mixing times the variations are small but not decreasing noticeably. These variations are sufficiently small that use of the procedure on an actual ship would not be compromised.

The AECL experiments have a Reynolds number approximately six times larger than that of the oil experiments. The change in Reynolds number seems to have had little effect on the results. A full size tank (12 m by 12 m by 12 m) carrying crude oil would have

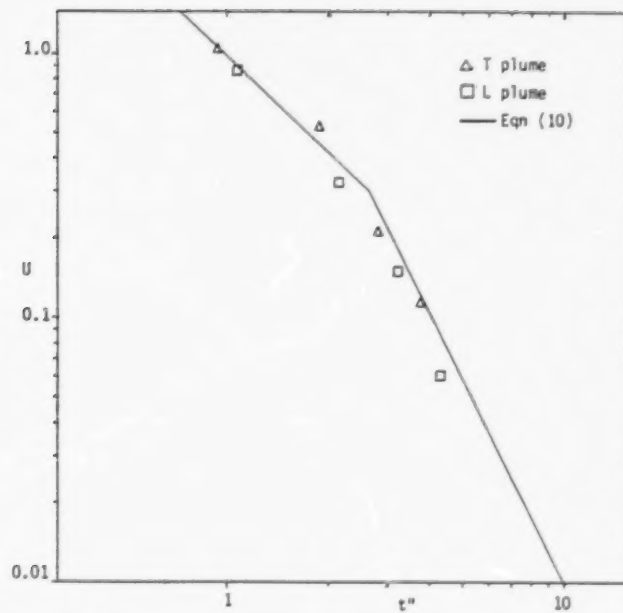


FIGURE 11

LOG-LOG PLOT U vs t'' FOR THE "L" and "T" PLUME DISTRIBUTION
PIPES WITH A DEPTH OF 1.22 m AND A GAS FLOW OF 0.48 LITERS/SECOND

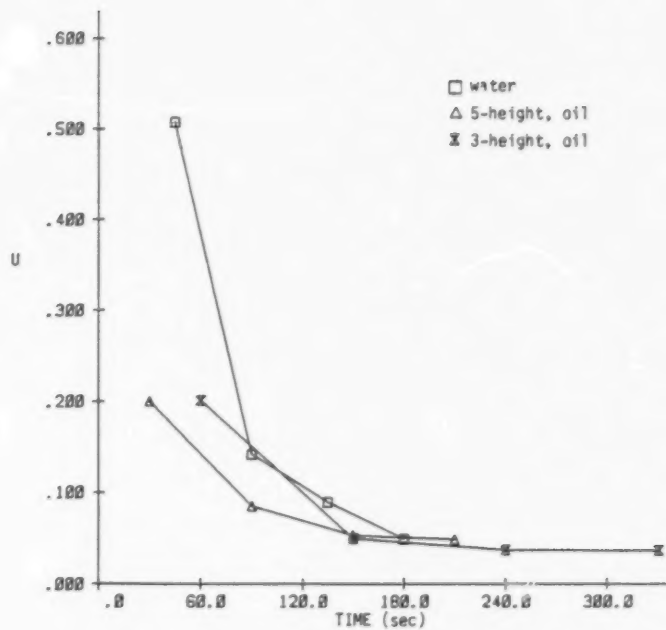


FIGURE 12

REDUCED DATA (U vs t) FOR THE STRAIGHT DISTRIBUTION
PIPE, GAS FLOW OF 0.6 L/s AND A FLUID DEPTH OF 1.22 METERS

Table 3. Percentage of Fully Mixed Concentration of the Grab Samples. Each group of samples were taken when a separate height was tested.

<u>Time (sec)</u>	<u>Percentage of Fully Mixed Concentration</u>		
30	165	129	157
60	87	68	89
90	99	77	79
120	90	87	93
150	100	93	100
180	96	95	100
210	99	95	104
240	99	94	100
270	97	96	100
300	97	90	99

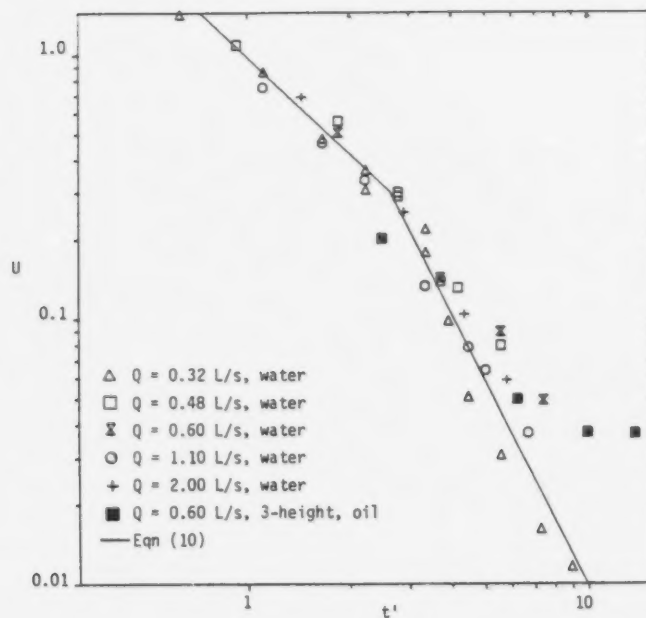


FIGURE 13

LOG U vs LOG t' FOR 1.22 METER FLUID DEPTH

a Reynolds number of not less than one third of the water experiments. Since a sixfold increase in the Reynolds number did not have an effect on the mixing it is unlikely that the mixing will be affected by such a small decrease in the Reynolds number.

CONCLUSIONS

The rapid mixing which can be achieved with bubble plumes can be characterized by equation (10) for square based tanks and a considerable range of liquid heights, gas flows and plume distribution pipe configurations. The only conditions under which the characterization of mixing vs the dimensionless time, t'' , failed to be accurate in our experiments are when the fluid depth and gas flow are both small conditions; conditions not likely to be found in applications. The most likely cause of this is the artifact of pre-mixing by the method of dye introduction. Since eq (9) predicts the mixing for three different overall flow patterns the equation may be applicable to a considerably broader range of conditions than we tested. For example, it might be applied to rectangular base tanks by substituting the base area for L^2 .

The characteristic mixing time T is a combination of the time it takes to supply on tank volume of gas, T_1 and the time it takes to circulate a tank volume of fluid through the plume, T_2 . On a logarithmic scale, T_1 contributes 20% of the mixing time and T_2 contributes 80%. T_2 is the more influential factor.

The steeper slope in U vs t'' for $t'' < 2.65$ can be interpreted as an increase in mixing that occurs once the fluid has passed through the plume several times and the large scale fluctuations have been eliminated.

Although the oil tests suffered from long sample acquisition times and a small excess dispersant concentration at long mixing times, the findings indicate that there are not any significant differences between oil mixing and water mixing. This applies to the high Reynolds numbers such as those used in both the water and the oil tests.

The values of U from the oil experiments agree with the results of the water experiments when t' is less than 10 and for larger dimensionless times U has a value of 0.037. This may be the result of not taking enough samples to determine U accurately or of errors in radioactivity measurements. However, any value of U less than 0.05 can be considered low enough to be ignored since in the anticipated mixing applications, the excess dispersant used would exceed 5% of the theoretical dispersant requirement.

The bubble plume proved itself to be an efficient mixer of rectangular tanks with the "T" plume being the fastest of the plume arrangements tested. On the basis of the experimental results, it is predicted that a plume 12 m long operating at a gas flow rate of $0.1 \text{ m}^3/\text{s}$ would mix a tank of 12 m length and width to an average concentration variation of 30% within four and one-half minutes if the dispersant was added instantaneously into the bubble plume region of the tank. Extra time required to add the dispersant could

act as a safety factor so that the total estimate of mixing time would be conservative.

ACKNOWLEDGEMENTS

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ALASKA CLEAN SEAS DEVELOPMENT OF A CHEMICAL APPLICATION MANUAL

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ABSTRACT

Alaska Clean Seas has sponsored the development of a chemical application manual which in its early form is primarily concerned with the operational aspects of dispersant application in the marine environment off Alaska. With specific guidelines and procedures for dispersant application, the manual is intended as a practical operational tool for advance planning and for real-time use in the event of an actual oil spill. The manual does not focus on the process of achieving regulatory approval for dispersant use, nor does it provide guidelines for evaluating environmental consequences of dispersant use. It does, however, provide specific information on the selection, use and availability of chemical dispersants, application equipment and platforms, logistics support services, and staging locations and facilities. Included in this paper is a summary of the objectives, scope and content of the chemical application manual. In addition, a mathematical model is described and used with typical dispersant application data to illustrate the importance of advance planning for the most practical and cost-effective means of applying dispersants.

BACKGROUND AND GENERAL CONTENT

This paper is a summary of a much more extensive report prepared by Spiltec for Alaska Clean Seas (ACS), an oil-industry-sponsored oil spill response organization based in Anchorage, Alaska. Technical support was provided by the ACS Dispersant Subcommittee, and the project was administered by Standard Alaska Production Company. The original report, Alaska Oil Spill Chemical Application Manual (Spiltec, 1986), contains the results of one of several R&D efforts sponsored by ACS during 1985.

Early planning for dispersant use or non-use is essential if adequate consideration is to be given to the full range of oil spill response options available following a spill. Without such planning, the spiller company, its contractor(s), the government On-Scene Coordinator (OSC), the Regional Response Team (RRT), etc. cannot consider in a timely manner the complexity of issues involved. This manual deals primarily with the operational aspects of dispersant application procedures and provides specific guidelines for chemical dispersant use in the marine environment off Alaska. The manual is intended as a practical operational tool for advance planning and for real-time use in the event of an actual oil spill. Updating of the manual may be necessary as a result of advances in dispersant application equipment and procedures, dispersant composition, and our understanding of the interactions of dispersants with oil and the environment. As product information becomes available and experience is gained in the use of other chemical products for spill control, the manual will be expanded to include such potential countermeasures.

The contents of the manual do not focus on the process of achieving regulatory approval for dispersant use, nor does the manual provide guidelines for evaluating environmental consequences of dispersant use. It does serve, however, as a reference manual, providing information and guidelines on the selection, use, and availability of:

- o Chemical dispersants,
- o Application equipment,
- o Application platforms (aircraft and vessels)
- o Logistics support services and personnel, and
- o Staging locations and facilities.

In addition, the manual includes an assessment of the key operational factors that would enter into a complete time and cost analysis of dispersant use. Analysis procedures and sample results are described to illustrate the importance of advance planning for the most practical means of dealing with various types and magnitudes of spillage.

The chemical application manual is intended primarily for use by the member companies of Alaska Clean Seas. It is recognized, however, that the manual provides useful guidelines and information for all individuals and organizations involved with the potential use of chemical dispersants for oil spill control.

The list below is representative of the information that can be found in the ACS manual:

- o Training material including general dispersant use guidelines, capabilities and limitations, and specific application procedures.
- o Regulatory input, equipment specifications, operational constraints, staging and logistics data, etc. to develop regional and site-specific oil spill contingency plans.
- o A comprehensive dispersant application model involving the many parameters that must be addressed to assess the most practical and cost-effective means of establishing an effective dispersant response capability.
- o Input for government/public relations and interfacing to achieve acceptance and cooperation in planning or implementing a dispersant use program.
- o Regional Response Team guidelines for the State of Alaska and preselected boundaries for potential use of dispersants.
- o Locations, contacts, and quantities of chemicals, equipment, and personnel for dispersant application operations at any number of staging areas.
- o Description and assessment of spill characteristics and dispersant application parameters to achieve proper dosages and to maintain an efficient ongoing dispersant operation.

- o Specific dispersant application systems and their recommended platforms (aircraft and vessels).
- o Dispersant product information including U.S. Environmental Protection Agency's (EPA's) National Contingency Plan Product Schedule, ACS Dispersant Data Sheets, manufacturers' brochures, Material Safety Data Sheets, etc.
- o Spill monitoring considerations including U.S. EPA's "Checklist For Dispersant Observations."
- o An extensive reference list of more than 130 documents consulted during the preparation of the manual. Where appropriate because of particular relevance to the subject of oil spill chemicals in cold climates, references have been briefly annotated to highlight key points.

SELECTED DISPERSANT APPLICATION CONSIDERATIONS

Logistics

The logistical aspects of a dispersant application program in Alaska are of paramount concern because of the size and remoteness of the offshore regions within which oil spills could conceivably occur. The choice of the optimum dispersant application platform, for example, will depend strongly upon the size and location of the spill to be treated. Other factors such as slick thickness and condition, wind and sea state, etc. are of course important; however, the decision to use a particular application platform will depend primarily upon the amount of oil to be dispersed and the distance of the oil from a suitable staging location.

Should a major spill occur, it may be impossible to treat a significant portion of the oil in a timely manner unless the payload per dispersant run (or sortie) is quite large. The proper treatment of a major spill may necessitate the use of large, multi-engine, fixed-wing aircraft in order to deliver a sufficient volume of dispersant within a reasonable time-frame. Such aircraft can normally achieve areal coverage rates that are 10 to 100 times greater than smaller aircraft and vessels for a given dosage requirement.

The dependence of an effective dispersant use operation on such factors as payload per sortie and platform range and coverage rate illustrates the importance of advance logistical planning. Available dispersant application aircraft and/or vessels will have to be considered carefully with respect to their maximum operating ranges, payloads, runway or dock needs, refueling and dispersant resupply requirements, personnel support and maintenance needs, etc. It is desirable, for example, that staging locations for large fixed-wing aircraft have available bulk storage and large pump-rate capabilities so that the turn-around time between sorties is kept to a minimum. In addition, primary staging locations should have facilities and equipment to support operations during limited visibility, night-time (for delivery of backup dispersants), and long-term response to an ongoing spill such as a blowout.

A comprehensive logistics plan will have to reflect the kinds and amounts of fuel needed for various delivery platforms, the type and location of heavy equipment necessary to transport and load dispersants, the food and housing requirements for support personnel, and the communications systems necessary to coordinate all onshore and offshore operations. Should vessel-mounted systems be employed, personnel, trucks and adequate roads will be necessary to transport dispersant between the airport and an adequate loading dock. Water depths at dockside will have to be sufficient for the vessel(s) under consideration, or alternate plans will have to address the feasibility of transporting dispersants via helicopter to the vessel off-shore.

Because of these and many other logistical considerations, the ACS Chemical Application Manual contains source lists and specific information on:

- o Dispersant manufacturer stockpiles and production rates;
- o Oil industry and contractor stockpiles of dispersants;
- o Chemical application spray systems;
- o Fixed-wing aircraft, helicopters, and vessels available for dispersant spraying;
- o Contractors that can provide aerial surveys, field sampling/ environmental surveys, laboratory analyses, etc.; and
- o Staging locations carefully selected for their potential utility in supporting an efficient offshore dispersant application program.

Fifteen primary staging locations were selected for Alaska, each one addressed in the manual with such data as:

- o Distances to lease sale areas and potential spill zones;
- o Airport and flight service information;
- o Fuel supply, bulk storage, pumps and general support services;
- o Port and dock facilities; and
- o Local weather patterns.

Dispersant Application Systems

Performance. By comparing the capabilities and limitations of various spray equipment and platforms (aircraft and vessels), one can evaluate the performance of each system for its practicality in meeting the space, time, and cost constraints of an effective response. Typical measures of such practicality include:

- o Areal coverage rate and spraying time per payload,
- o Number of sorties and time to treat a given portion of the spill,
- o Volume of dispersants needed, and
- o Dosage levels achievable with each system.

In a given spill situation, the feasibility of a particular dispersant application system can be assessed by comparing these estimates with the time anticipated for the oil slick to reach a specific location and/or condition (e.g., size, patchiness, or thickness). In addition, the dosage achievable with each system can be compared with the anticipated dosage requirements.

Many other factors must also be considered when examining the practicality and/or the state-of-readiness of a specific dispersant application system. These factors include:

- o Materials, personnel and time required to modify any parts of the system for a particular spray pattern or dosage;
- o Any delays that may result because new aircraft or vessels-of-opportunity must be used or because calibration tests must be completed;
- o Any special requirements for fuel, maintenance, and other ground support;
- o The existence of flow meters or calibrated pumps to provide positive control of dispersant usage; and
- o The proper type, size, number, and orientation of nozzles to meet the requirements for a particular dosage, ground speed, or differential velocity requirement.

A major portion of the manual is devoted to a thorough analysis of the operational parameters commonly used to estimate areal coverage rates, dosage requirements, spraying times, etc. Figure 1 expresses the relationship among most of the key dispersant application parameters. (The figure is given in English units, which are currently preferred by ACS member companies.)

Figure 1 was used to examine and compare many of the performance characteristics of various dispersant application platforms. Table 1 provides a summary of such performance estimates for the four primary spray platforms addressed in the manual (large and small fixed-wing aircraft, helicopters and vessels).

Using Table 1, a simplified performance summary was developed (Table 2) in which key operating characteristics for each platform classification are presented as very rough (order-of-magnitude) estimates. These approximations are quite useful, however, in making quick judgements about the relative merits of each platform type for a particular spill scenario. For example, Tables 1 and 2 reveal the following:

- o Large, multi-engine, fixed-wing aircraft can achieve areal coverage rates that are typically 100 times greater than those for vessels and about 10 times faster than for most small single-engine aircraft and helicopters.

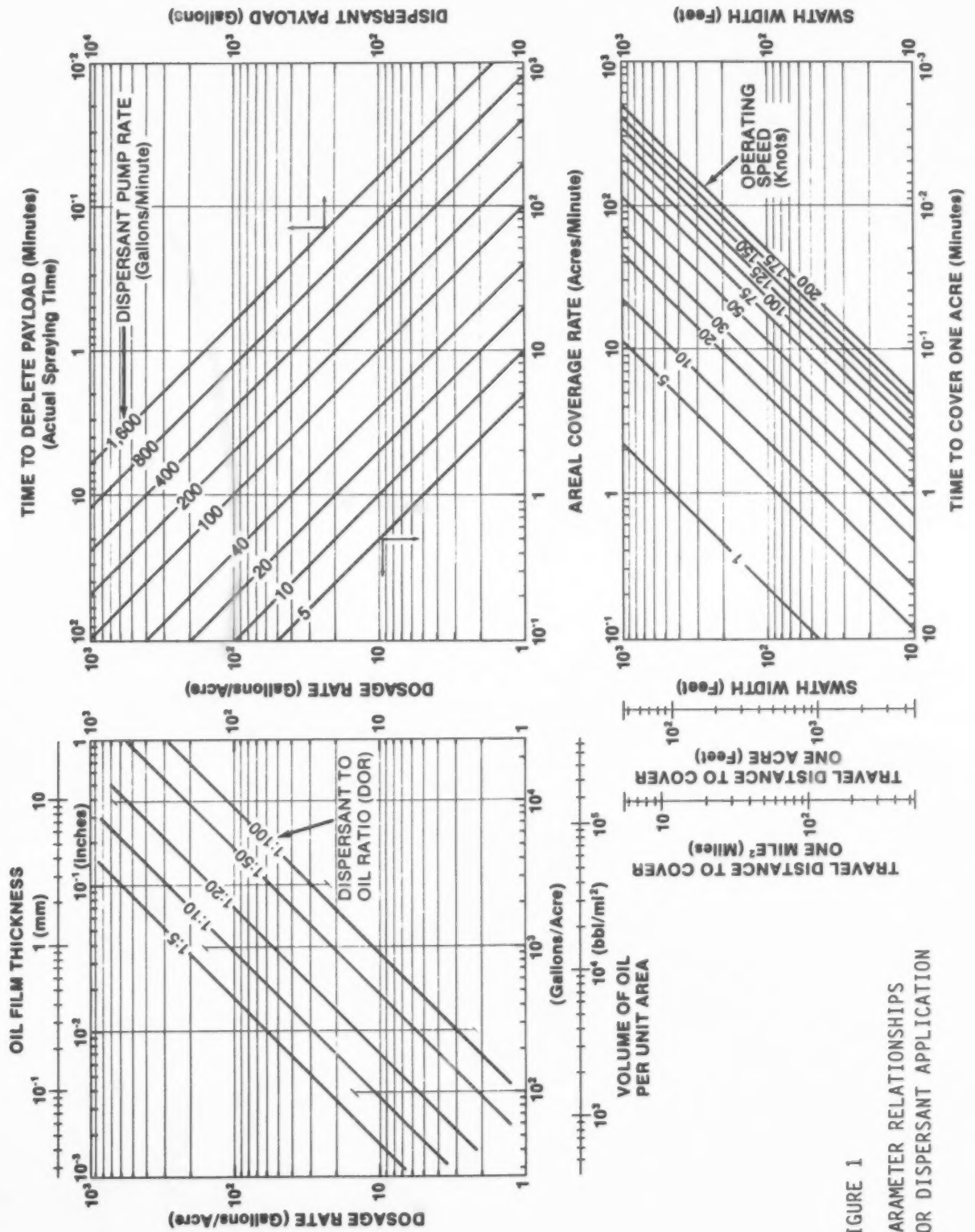


FIGURE 1
PARAMETER RELATIONSHIPS
FOR DISPERSANT APPLICATION

TABLE 1
DISPERSANT APPLICATION PLATFORMS - TYPICAL OPERATING CHARACTERISTICS

	DISPERSING SWATH WIDTH (Feet)	DISPERSING SPEED (Knots)	DISPERSANT PAYLOAD (Gal)	DISPERSANT PUMP RATE (gpm)	RANGE ONE-WAY WITH FULL LOAD (Naut. Miles)	TRANSIT SPEED (Knots)	MINIMUM RUNWAY LENGTH REQUIRED (Feet)	AREAL (a) COVERAGE RATE (Acres/Min)	TIME (b) TO DEplete PAYLOAD (Min)	AREA (c) OF OIL DISPERSED PER PAYLOAD (Acres)
LARGE MULTI-ENGINE AIRCRAFT	100 to 200+	125 to 175	2,000 to 5,500	100 to 900	350 to 700	175 to 260	5,000	25 to 100+	3 to 15+	75 to 1,500+
SMALL SINGLE-ENGINE AIRCRAFT	40 to 60	60 to 80	100 to 300	40 to 100	75 to 150(d)	80 to 100	2,000	5 to 11	2.5 to 3	12.5 to 33
HELICOPTERS	50 to 80	40 to 80	100 to 600	40 to 120	40 to 120(e)	80 to 100	Not Applicable	5 to 15	3 to 5	15 to 75
VESSELS	40 to 100	5 to 10	100's to 1,000's	5 to 20	Many to 100's	10 to 20	Not Applicable	1/2 to 2	100's to 1,000's	100's to 1,000's

(a) Areal Coverage Rate (acres/min) = $\frac{\text{Velocity (kt)} \times \text{Swath (ft)}}{430}$

(b) Time to Deplete Payload (min) = $\frac{\text{Payload (gal)}}{\text{Pump Rate (gpm)}}$

(c) Area per Payload (acres) = [Areal Coverage Rate (acres/min)] x [Time to Deplete Payload (min)]

(d) Realistically range over water, especially in Alaska, is limited by safety considerations. Single-engine aircraft are normally not operated beyond gliding distance from shore.

(e) Range of single-engine helicopters may be more limited for safety reasons.

TABLE 2

SIMPLIFIED PERFORMANCE SUMMARY FOR DISPERSANT APPLICATION PLATFORMS

	AREAL (a) COVERAGE RATE (Acres/Min)	TIME TO DEplete PAYLOAD (Min)	AREA OF OIL DISPERSed PER PAYLOAD (Acres)	MAXIMUM OPERATING DISTANCE FROM STAGING AREA (Naut. Miles)	TYPICAL DOSAGE ACHIEVABLE WITH EQUIP. COMMONLY USED (Gal/Acre)	ESTIMATED SPRAYING TIME TO TREAT 1 SQUARE MILE (Not including Transit, Repositioning, Refueling, etc.)	MANEUVERABILITY FOR DISPERSING PATCHY/ IRREGULAR SLICKS	TYPICAL (d) VOLUME OF OIL DISPERSed PER PAYLOAD ASSUMING DOR OF 1:20 (Barrels)
LARGE MULTI-ENGINE AIRCRAFT	100	<10	100 to 1,000+	>200	2 to 20	<10 min. (1 to 3 Payloads)	Poor	100's to 1,000+
SMALL SINGLE-ENGINE AIRCRAFT	10	<3	10 to 30	Variable (typ. <10)	2 to 10	≈ 1 hour + (20 Payloads)	Fair	50 to 150
HELICOPTERS	10	<5	10 to 100	Variable (typ. <10)	2 to 25 ^(b)	≈ 1 hour (6 Payloads)	Excellent	50 to 280
VESSELS	1	100's to 1,000's	100's to 1,000's	Variable ^(e)	2 to 80 ^(c)	≈ 10 hours (1 Payload)	Good	100's to 1,000's

(a) Order-of-magnitude estimate

(b) Based on minimum dispersing speed of 40 kt

(c) Based on minimum dispersing speed of 5 kt

(d) Based on range of payload capabilities given in Table 6-1

(e) Depends on size of vessel

- o The areas that can be treated with dispersants from a single payload are typically 10 to 100 times greater with large aircraft and vessels than with small aircraft and helicopters.
- o The dispersing and transit speeds for large, multi-engine aircraft are 2 to 3 times faster than for small fixed-wing aircraft and helicopters, and at least 10 times faster than for most vessels.
- o While both large aircraft and vessels can carry comparable payloads, the time required to treat one square mile may be less than 10 minutes by air and more than 10 hours by boat.
- o Most application systems can deliver dosages in the 2 to 10 gal/acre range with standard off-the-shelf equipment if properly operated. Helicopters and vessels, however, can increase dosages as necessary by decreasing speed while spraying. Boats can also carry much larger pumps quite easily (or use firefighting systems) to achieve even higher dosages.
- o Large aircraft and vessels provide relatively stable platforms with good endurance and safety features compared to small aircraft and helicopters for offshore operations. In Alaska, small aircraft and helicopter operations with dispersants may be limited to Cook Inlet and nearshore waters only.
- o Since helicopters provide the best maneuverability for dispersing patchy/irregular slicks, their operating range could be extended using large, multi-engine helicopters. Helicopter operations could also be supported at sea by using an exploration or production platform with a helo-pad, or a barge and a helo-pad along with a stockpile of dispersants.

Using the dispersant application model mentioned earlier, the ACS manual includes some important assessments of how various spray aircraft and vessels are affected by the distance between the platform's staging location and the spill being treated. To illustrate the value of such an analysis, Figures 2 and 3 have been reproduced here to show how the time per sortie and the area covered in a 10-hour day might change with the distance to a spill. The plots for the designated spray platforms are based on an assumed 15 gal/acre (140 liters/hectare) dosage and on areal coverage rates ($\dot{A}$), areal coverages per payload (A_p) and other simplified performance characteristics noted in the figures.^p The dosage of 15 gal/acre is arbitrarily selected to be representative of what could be required for a spill with an average thickness on the order of a hundredth of an inch (assuming a dispersant-to-oil ratio of 1:20). These plots provide examples of the kinds of data that could be developed in advance for specific application platforms and dispersant application criteria that might actually be used in a given region.

The data presented in Figures 2 and 3 serve to identify many important relationships among typical platforms that could be available for dispersant use. Most large vessels, for example, will very likely require several

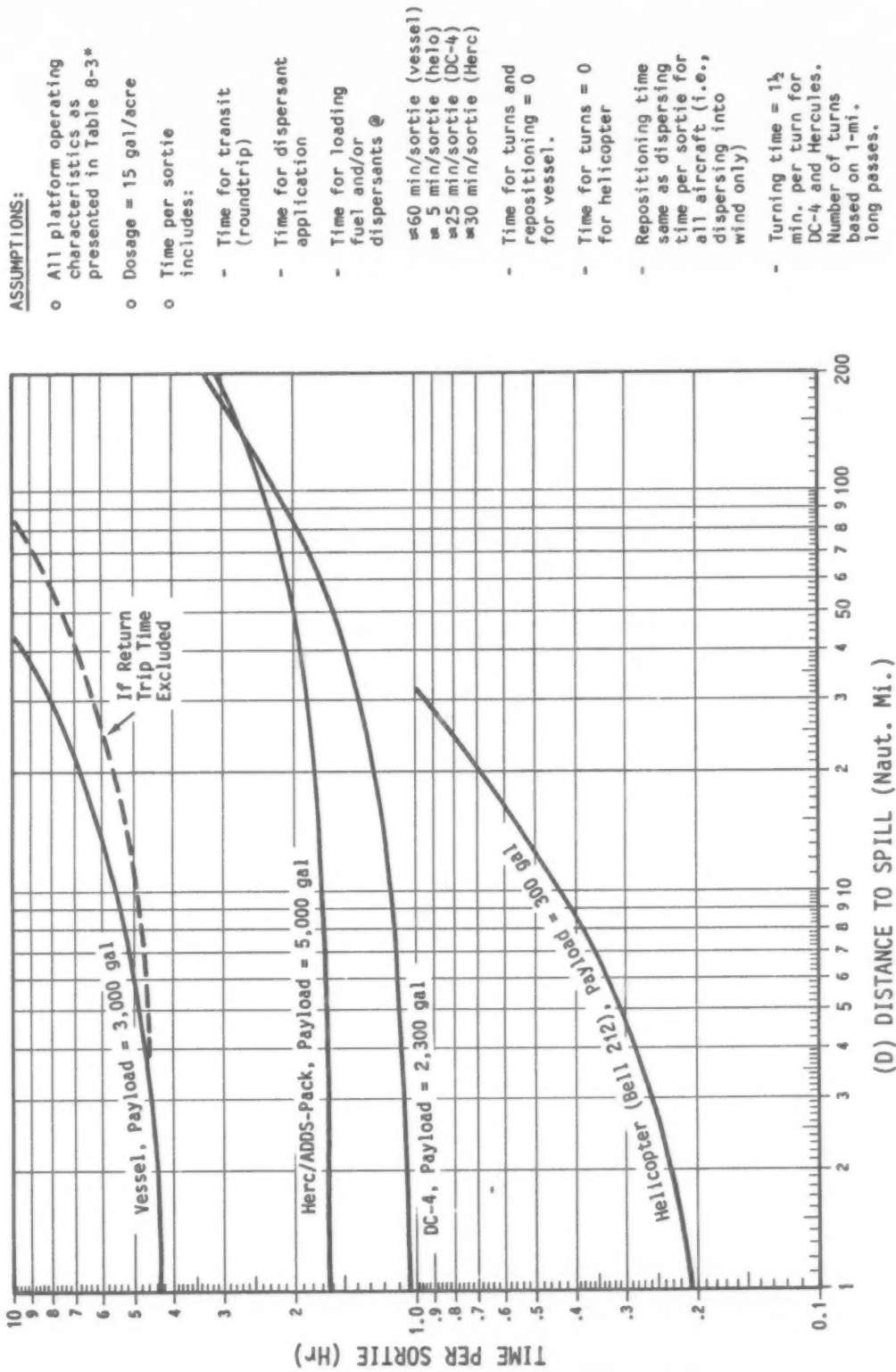


FIGURE 2 TIME PER SORTIE VS DISTANCE TO SPILL
FOR TYPICAL AIRCRAFT AND VESSEL DISPERSANT APPLICATION SYSTEMS

* Nominal operating characteristics were used; see Table 8-3 in original report for details (Splitec, 1986)

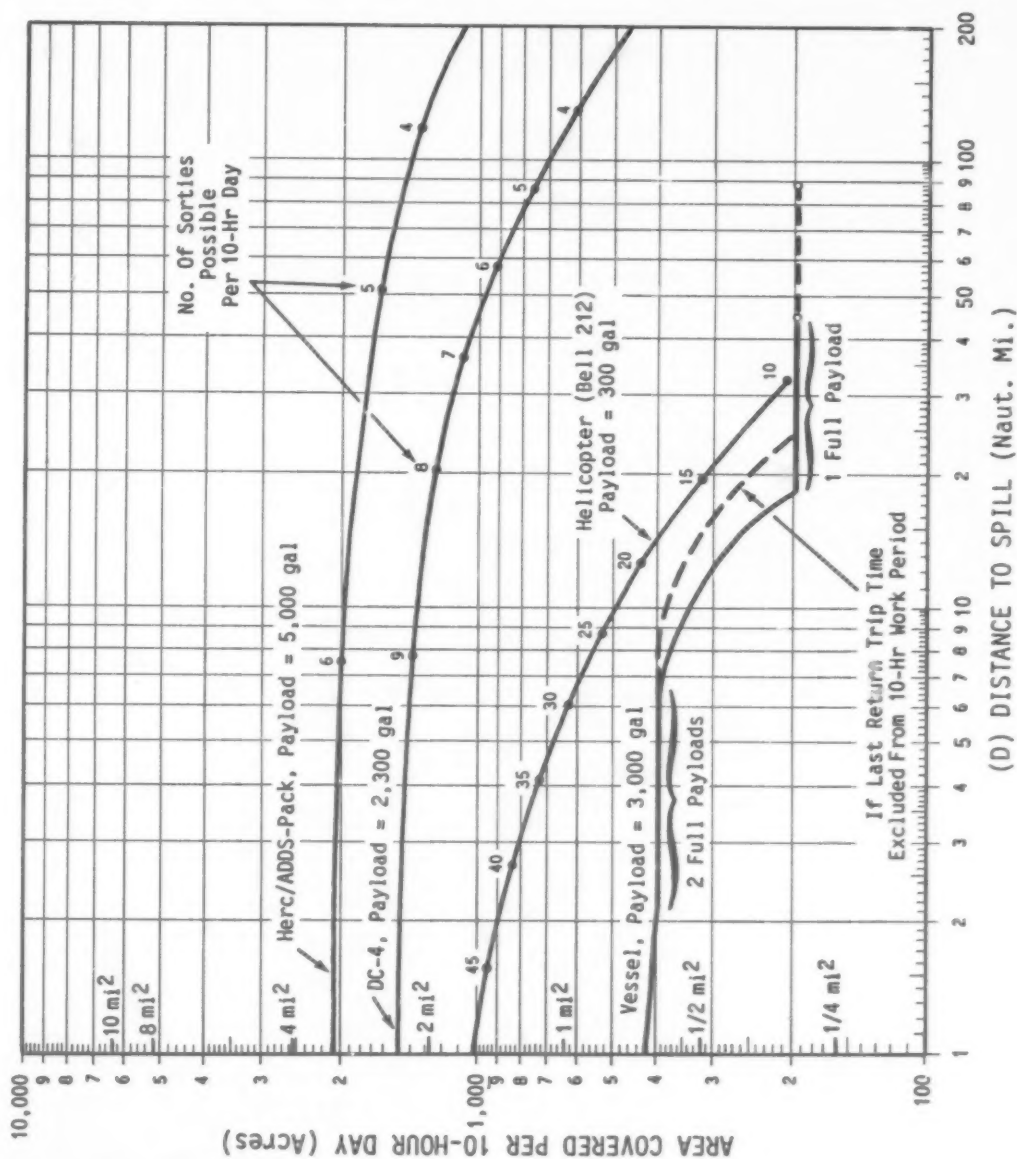


FIGURE 3 AREAL COVERAGE CAPABILITY VS DISTANCE TO SPILL
 FOR TYPICAL AIRCRAFT AND VESSEL DISPERSANT APPLICATION SYSTEMS

hours to complete a single sortie involving thousands of gallons of dispersant. Compared to fixed-wing aircraft with comparable payloads, the vessel could require nearly 10 times as much time to cover only a tenth of the area achievable with the aircraft. In a 10-hour working period, the large, relatively fast vessel used in this example could deliver only 2 payloads of 3,000 gal each to spills less than 7 to 8 naut. mi. from its staging location. If only 1 full payload in 10 hours is sufficient, the same vessel could reach spills nearly 90 naut. mi. away (excluding the time to travel back to base).

Under the assumptions provided, a Bell 212 with 300 gal/payload could conceivably treat spills as far away as 33 naut. mi. Such treatment, however, would be limited to approximately 10 sorties per 10-hour day, involving little more than about 200 acres. The same helicopter spray system could reduce its time per sortie to about 15 minutes by working on spills no farther than a few miles from its staging location. In this situation, the helicopter could effectively treat 800 to 1,000 acres per 10-hour day, accomplishing as many as 40 to 50 sorties.

The relative insensitivity of large fixed-wing aircraft to transit distance (D) is illustrated by their nearly horizontal plots out to approximately 50 naut. mi. in Figures 2 and 3. The DC-4 and the Hercules maintain relatively short completion times per sortie (less than 2 hours) to the 50-naut.-mi. distance (base to spill), and these times increase only slightly to about 3 hours at 200 naut. mi. from base. With such short times per sortie, these aircraft can deliver as many as 3 to 5 payloads hundreds of miles from their staging locations in less than 10 hours.

Available Application Equipment. The ACS chemical application manual includes a section with detailed operating specifications and performance data for a number of fixed-wing aircraft, helicopters, and vessel-mounted spray systems. Included are:

o Fixed-Wing:

- DC-4 and spray system
- DC-6B and spray system
- Lockheed Hercules (L-100, C-130) and Airborne Dispersant Delivery System (ADDS)

o Helicopters*

- Hughes 500D
- Bell 206-B (Jet Ranger)
- Bell 206-L (Long Ranger)
- Aerospatiale AS 350 (Astar Mark III)
- Bell 205A-1 (Huey)
- Bell 212
- Bell 412
- Aerospatiale AS 332L (Super Puma)

* Including Evergreen and Simplex helicopter spray systems.

o Surface Systems:

- ARCAT Dispersant Spray System
- SLICKBAR Mini-Dispersant Spray System
- SPILLSPRAY Meter-Controlled Dispersant Spray Unit

While many other aerial and surface spraying systems exist, the manual is currently focusing on those equipment and application platforms that are presently located (or rapidly accessible) within Alaska.

Exhibit 1 on the following four pages, which are taken from the manual, covers the Lockheed Hercules and ADDS and illustrates the format and level of information given for each of the above dispersant application systems. Note that Figure 7-6 on the last page of the exhibit is basically the same as Figure 1; however, the range of typical operating conditions is shaded for easy reference.

SUMMARY STATEMENT

The Alaska Oil Spill Chemical Application Manual described in this paper is one of many documents used by Alaska Clean Seas for contingency planning and training for spill response in the arctic and subarctic waters surrounding Alaska. The manual was published in looseleaf format to facilitate future revisions to keep pace with technological and regulatory developments.

REFERENCE

Spiltec, 1986. Alaska Oil Spill Chemical Application Manual. Prepared under contract to Standard Alaska Production Company for Alaska Clean Seas, Anchorage, AK.

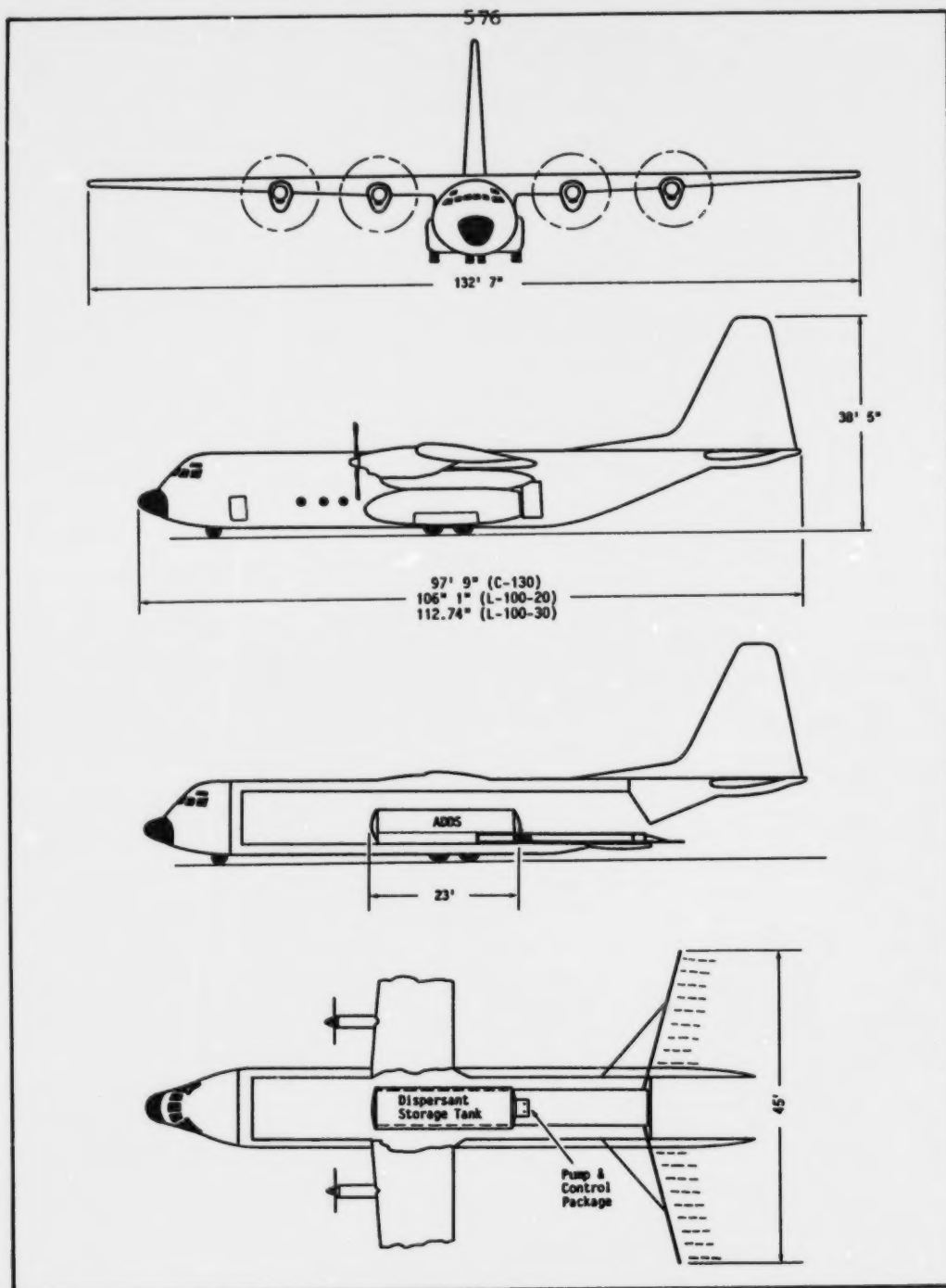


FIGURE 7-5 LOCKHEED HERCULES WITH ADDS PACK

EXHIBIT 1

SAMPLE DESCRIPTION OF DISPERSANT APPLICATION SYSTEM
FROM ACS ALASKA OIL SPILL CHEMICAL APPLICATION MANUAL

FIXED-WING AIRCRAFT

LOCKHEED HERCULES*

AIRCRAFT SPECIFICATIONS

Propulsion System.....4 Allison turboprop engines
 Fuel Required.....Jet
 Fuel Capacity (depends on tank configuration).....7,000 to 9,000 gal
 Average Fuel Consumption Rate.....750 gal/hr

AIRCRAFT PERFORMANCE

Maximum Takeoff Gross Weight (MTOW).....155,000 lb
 Average Empty Weight.....80,000 lb
 Average Useful Load.....75,000 lb
 Normal Cruise Speed.....300 kt
 Endurance Without Load.....12 hr
 Endurance With Full Load.....4 hr
 Minimum Runway Length at Sea Level (with full load).....4,500 ft

SOURCES

MARKAIR, INC., P.O. Box 190769, Anchorage, AK 99519-0769
 (907) 243-1414

Operates three L-100-30 aircraft

SOUTHERN AIR TRANSPORT, INC., P.O. Box 52-4093, Miami, FL 33152
 (305) 871-5171, (800) 327-6465, Telex: 51-8856

Operates four L-100-30 aircraft and two L-100-20 aircraft. Only
 L-100-20 aircraft are ADDS capable

TRANSAMERICA AIRLINES, P.O. Box 2504, Oakland International Airport,
 Oakland, CA 94614, (305) 871-5171, Telex: 52-8856

Operates twelve L-100-30 aircraft and one L-100-20 aircraft. At
 least three aircraft are ADDS capable

* L-100 is manufacturer's designation, with -20 and -30 suffixes
 identifying model series. L-382 is FAA designation of aircraft type.
 C-130 is designation of military version.

FIXED-WING AIRCRAFTAIRBORNE DISPERSANT
DELIVERY SYSTEM (ADDS)SPRAY SYSTEM SPECIFICATIONS

Maximum Dispersant Payload.....5,500 gal
Dispersant Pump Rates.....100 to 800 gpm
ADDS Dry Weight.....4,500 lbs
Dual Centrifugal Pumps (with full remote control from cockpit)

PERFORMANCE (with Hercules)

Effective Swath Width.....150 to 200+ ft
Installation/Removal Time.....approx. 15 min
Normal Cruise Speed (transit speed).....260 to 300 kt
Dispersant Spraying Speed.....130 to 150 kt
Areal Coverage Rate.....45 to 70+ acres/min
Possible Dosage Rates.....approx. 1½ to 18 gal/acre
Approximate Spraying Time Per Payload.....7 to 55 min
Potential Volume of Oil Dispersed per Payload
(assuming a dispersant-to-oil ratio of 1:20).....2,600 bbl

SOURCE

BIEGERT AVIATION, INC., Memorial Airport, 22022 S. Price Road, Chandler,
Arizona 85224 (Telex: 165775), James C. Jeffries, (602)
895-0441

Maintains at least one system on hand for sale or lease.

NOTE

Spray pumps cannot be used to onload dispersant chemical. Biegert has pumps, hoses, and fittings available for this purpose (not part of ADDS Pack).

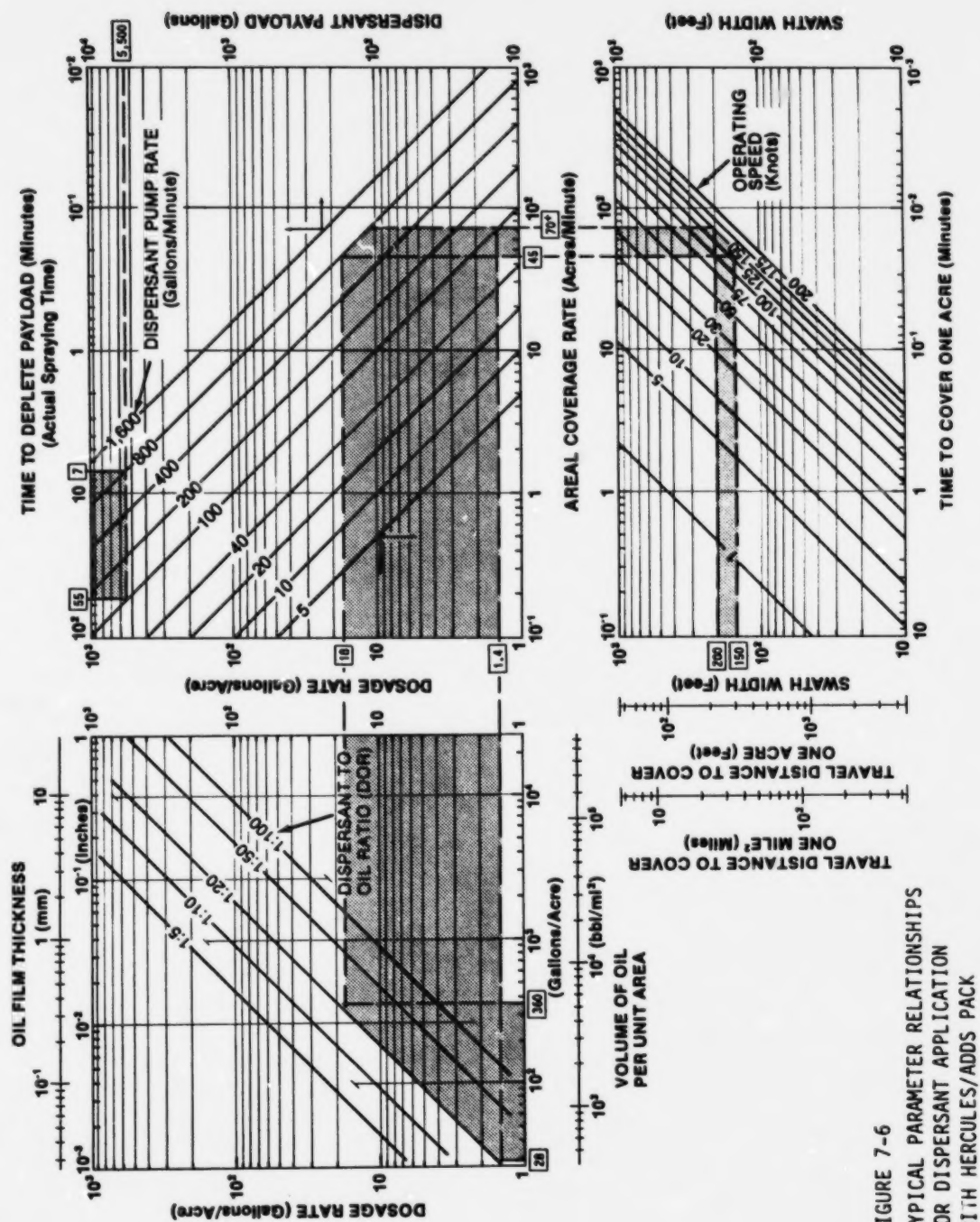


FIGURE 7-6
TYPICAL PARAMETER RELATIONSHIPS
FOR DISPERSANT APPLICATION
WITH HERCULES/ADDS PACK

DISPERSANT USE GUIDELINES FOR COOK INLET, ALASKA

Paul O'Brien¹, Carol-Ann Manen², Brad Hahn³, Howard Metsker⁴, Lyle Fox, Jr.⁵, David Kennedy⁵, Charles Getter⁵, Lynn Tomich⁶, LCDR Michael A. Conway⁷, and Lori Harris⁵

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INTRODUCTION

In early 1984, an Alaska Regional Response Team (RRT) working group, composed of representatives from the U.S. Coast Guard, U.S. Environmental Protection Agency, National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, and the State of Alaska, began developing dispersant use guidelines for Alaska. This work has culminated in the following draft guidelines for Cook Inlet, which have not been presented to the full RRT for final approval. Final guidelines should be ready for review and approval by the RRT in August 1986. It is anticipated that the RRT working group will begin developing dispersant use guidelines for other offshore areas, including Prince William Sound and the Beaufort Sea, after the Cook Inlet guidelines have been approved.

BACKGROUND

The capability to adequately respond to an oil spill in Alaska can be hampered by the great distances involved, poorly developed transportation networks, an inadequate labor force, limited mechanical spill cleanup technology, and severe weather conditions. The use of oil dispersing chemicals provides a supplemental response method to existing conventional cleanup techniques and allows spill response personnel some additional control over the type and location of spill impacts. However, dispersants, as a tool to mitigate the effects of oil spills in the environment, will be considered as a possible response option only when mechanical containment and recovery response actions are not workable.

Oil spill "dispersants" are complex chemical formulations consisting of a blend of surfactants, or detergents, in a mixture of solvents. Dispersants, when applied to a slick of floating oil, reduce the interfacial tension between oil and water and thus allow the oil to be broken into small droplets by the action of wind, waves, and currents. This process disperses oil into the water column and reduces hydrocarbon concentrations on the water surface.

Dispersant use is an important issue in Alaska because Alaskan marine waters support extremely valuable commercial, subsistence, and recreational fisheries; large and important populations of birds and mammals; and a growing oil industry. Since dispersants can be utilized to mitigate the extent of oil spill impacts, specific resources can be protected, if necessary. For example, some resources such as birds are known to be more vulnerable to spilled oil than others, an acceptable compromise may be to protect these resources by dispersing an oil slick in a less sensitive, deep water environment. In general, the compromise that must be evaluated is between the short-term impacts of introducing dispersed oil into the upper water column, and the long-term impacts of allowing oil to continue to float on the water surface and/or strand. In many cases,

adverse effects from chemically dispersed oil are much less than those that result from stranded oil in biologically sensitive areas, or to sea birds or marine organisms that float at the water surface, such as some fish eggs.

Dispersants, to be effective, must be applied in a timely manner; oil allowed to weather on the ocean surface becomes difficult, if not impossible, to disperse chemically. At present, as authorized by the National Oil and Hazardous Substances Contingency Plan, the U.S. Coast Guard On-Scene Coordinator (OSC) may use dispersants in response to a spill that endangers human life, or to prevent or substantially reduce hazard to human life. Alternatively, the OSC, with the concurrence of the U.S. Environmental Protection Agency (EPA) representative to the Regional Response Team (RRT) and the State of Alaska, may use those dispersants on the EPA acceptance list to mitigate the effects of spilled oil. In either case, the OSC must examine conventional response alternatives, such as containment and cleanup, for comparison to dispersant application (Appendix A). Dispersant use would be considered only when an effective conventional response is not feasible. Figure 1 outlines the logic used by the OSC to determine the feasibility of chemically dispersing oil spills in environmentally sensitive areas. This decision logic is detailed in the Alaska Regional Contingency Plan.

These guidelines, which are also part of the Alaska Regional Contingency Plan, and as such, subject to periodic review and update, are designed to streamline and expedite the decision-making process. They allow the timely and effective use of dispersants as an oil spill response tool to minimize environmental impacts. The guidelines are to be in force for the application of dispersants in any marine waters of Alaska.

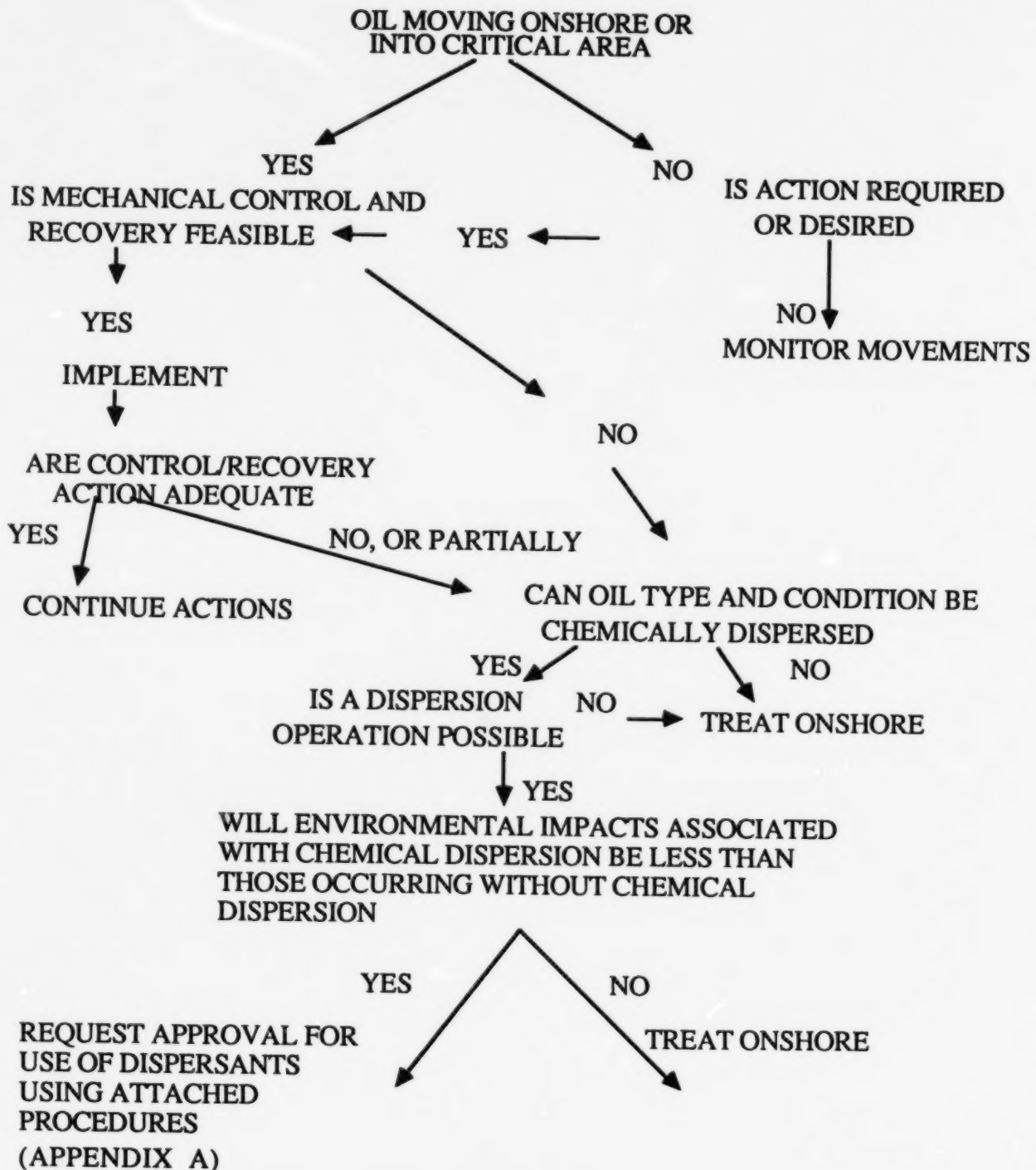
EFFECTS OF DISPERSANTS

Decisions concerning potential dispersant use must be based on an evaluation of potential impacts from dispersed versus undispersed oil since dispersing a slick at one site introduces more oil into the water column than would be caused by a surface slick. This means that effects on water column organisms may be increased at one site so that effects can be decreased or eliminated at other sites. Examples of such compromises include untreated oil threatening highly aggregated populations of surface utilizing organisms (migrating or staging populations of seabirds, breeding sites of birds or mammals) or particularly oil-sensitive coastal areas (spawning, nursery or feeding areas for fish, salt marshes, seagrass beds), and dispersed oil threatening aggregated populations of water column organisms (migrating salmon, fish or crab eggs or larvae).

The effects of oiling on marine birds and fur-bearing marine mammals are well-known; the extremely long residence time of stranded oil and the resulting high probability of chronic impact on both the subtidal benthos and the water column have been illustrated by the Baffin Island Oil Spill experiment (Boehm, 1983). Alternatively, the effects of chemically dispersing oil into the water column are transient but may be severe.

For the most sensitive organisms, exposure to hydrocarbon concentrations greater than 0.1 ppm for 96 hours may result in the death of 50% or more of the exposed organisms (Moore and Dwyer, 1974, corroborated for Alaskan species by Rice et al., 1984); exposure to similar concentrations for lessening periods of time usually results in declining mortalities. Zooplankton, specifically crustacean larvae and pelagic fish eggs and larvae, are among the most sensitive organisms and will suffer the largest mortalities. Larger and non-surface layer-dwelling organisms will suffer lesser mortalities.

Concentrations of dispersed oil of 100-1,000 parts per million (ppm) can be achieved in theory by mixing a slick of 0.1-1 mm in thickness completely into a static water column one meter deep (Table 1). In an actual situation, the water column would not be static, and vertical and horizontal diffusion would rapidly dilute the dispersed oil. In a series of field experiments performed off the coast of New Jersey, a dispersed oil concentration of 100+ ppm was measured in the top one-third meter of the water column one minute after application of the chemical dispersant. A second measurement made one hour after dispersant application indicated that this concentration had declined to 5 ppm. At one meter deep in the water column, the maximum concentration of



NOTE: Immediate threat to life PRE-EMPTS the necessity to use this matrix.

Figure 1. Dispersant Use Decision Matrix. (These Questions Must be Answered Before Deciding to Use Dispersants.)

dispersed oil measured was 30 ppm. At all depths, the measured concentration of dispersed oil declined rapidly until it was almost undetectable at 5 hours after dispersant application (Figure 2; Mackay and Wells, 1983; McAuliffe et al., 1980).

The toxicity of the dispersants presently stockpiled for use in marine waters is low, compared to that of petroleum hydrocarbons. For most of the dispersants presently on the EPA acceptance list, concentrations of 1 to 30 ppm were lethal to 50% of *Mysidopsis bahia*, a crustacean zooplankter, exposed to that concentration for 96 hours (Table 2). *M. bahia* is an excellent organism to use in toxicity assays as it is extremely sensitive. Other marine organisms exhibit LC₅₀'s ranging up to 100,000 ppm for these same dispersants (Table 3). In any case, the possibility of exposing organisms to concentrations of 1 ppm (or greater) of dispersants or dispersed oil for 96 hours, as the result of the dispersion of a real spill, is moderate to low. This is dependent on the size of the slick treated and the vertical and horizontal diffusivities in the water under and around the slick.

The Baffin Island Oil Spill (BIOS), an experimental oil spill designed to examine the "worst case" effects of dispersant use on the biota of nearshore areas in the Arctic, released chemically dispersed oil from a diffuser pipe placed near the bottom of the study bay. Concentrations of dispersed oil exceeding 160 ppm were measured at one point during this release. More widespread and sustained concentrations of 50 ppm for four to five hours rapidly declined to 0.03-0.05 ppm (Figure 3). Subsequent examination and long-term monitoring over a three year period of the benthic community in this bay revealed that, while there was some stressing of the organisms as indicated by gaping clams immediately after the spill, chemically dispersed oil concentrations of this magnitude and duration had no significant long-term effects on the sediments or the biota (Cross et al., 1984). In comparison, a similar amount of oil allowed to strand without treatment on the beach of a nearby bay is gradually leaching off the beach into the subtidal area, where it is being accumulated by the benthic organisms.

Table 1. Concentrations of dispersed oil in water as functions of oil thickness and water depth.

Appearance of oil on water	Approximate oil thickness (mm)	Concentration of dispersed oil in water (ppm) if uniformly mixed, when the water depth is:				
		1 m	2m	5m	10m	20m
Barely visible	4×10^{-5}	0.04				
Silvery sheen	8×10^{-5}	0.08	0.04			
First trace of color	1.5×10^{-4}	0.15	0.08	0.03		
Bright bands of color, iridescent	3×10^{-4}	0.3	0.15	0.06	0.03	
Colors tend to be dull	1×10^{-3}	1.0	0.5	0.2	0.1	0.05
Colors are fairly dark, little evidence of rainbow tints	2×10^{-3}	2.40	1.0	0.4	0.2	0.1
Brown or black	0.01	10.0	5.0	2.0	1.0	0.5
Black/dark brown	0.1	100.0	50.0	20.0	10.0	5.0
Black/dark brown	1.0	1000.0	500.0	200.0	100.0	50.0

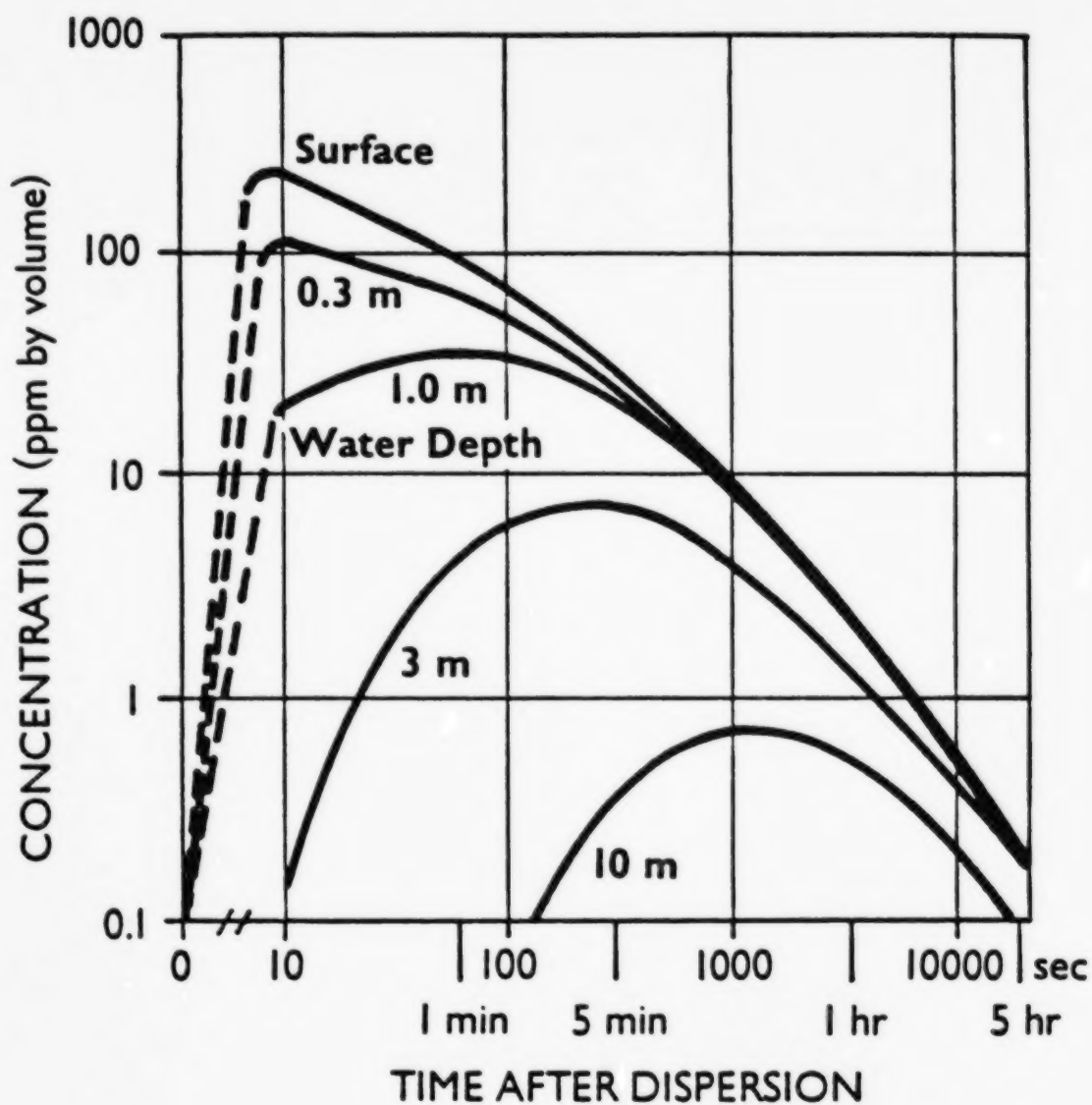


Figure 2. Illustrative plot of total concentration of oil under a slick formed from 100 barrels of dispersant-treated oil at stated depths as a function of time (Mackay and Wells, 1983).

Table 2. Relative effectiveness and toxicity of some chemical dispersants on U.S. Environmental Protection Agency approval list to *Mysidopsis bahia*, a crustacean zooplankter (Anderson et al., 1985).

dispersant	(15°C) dispersant:oil ratio (DOR90)*	(25°C) 96-h LC ₅₀ ppm
Atlantol AT-7	0.130	6.6
BP1100WD	0.009	1.4
Finsol OSR-7	0.038	204.0
Arcochem D-609	0.007	29.0
Corexit 9527	0.009	31.9
Corexit 7664	0.500	515.0
Corexit 8667	0.028	2.0
Petrocon N/T#4	0.018	15.0
Ameriod OSD/LT	0.110	6.7
Slick-A-Way	0.240	16.0
Conco K	0.580	3.5
BP1100X	0.150	17.0
Magnus Maritec	0.012	8.0
Petromend	0.008	3.7

*DOR₉₀ is the ratio of dispersant to oil required to disperse 90% of the oil (i.e., a low ratio indicates high effectiveness).

GENERAL ALASKA DISPERSANT USE CRITERIA

The dispersant use criteria developed for Alaska classify coastal waters into three dispersant use zones. In all cases, the use of dispersants will be based on the determination that the impact of dispersants or dispersed oil will be less harmful than non-dispersed oil. These zones are defined by: 1) physical parameters such as bathymetry and currents; 2) biological parameters such as sensitive habitats or fish and wildlife concentration areas; 3) nearshore human use activities; and 4) time required to respond.

Zone 1

The use of dispersants in Zone 1 is acceptable and should be evaluated, after consideration of mechanical means, as a response tool to mitigate oil spill impacts. The OSC is not required to obtain approval from EPA or the State of Alaska prior to the use of dispersants in this zone. However, the OSC will notify EPA and the State of the decision as soon as practicable.

Zone 1 is defined as an area in which dispersant use should be considered as a means to prevent or reduce the amount of oil reaching the shoreline or other sensitive resources, including:

- a) endangered or threatened species protected by Federal and State governments;
- b) nesting, spawning, breeding, and nursery areas for mammals, birds, fish, and shellfish;
- c) fish and wildlife concentration areas where these animals feed, rest, or migrate;
- d) sensitive marine habitats, including:
 - a. seagrass beds
 - b. kelp beds
 - c. shellfish beds

Table 3. Acute Lethal Toxicity of Some Oil Spill
Dispersants to Marine Organisms--A
Selection of Current Data (modified Wells, 1984).

Species/Stage	Dispersant	Threshold Concentrations Expressed as Four-Day LC ₅₀ 's, ppm ^a
Invertebrates		
Stony coral (<i>Madracis mirabilis</i>)	Shell dispersant LTX [*]	162 (1 day)
Oligochaete (<i>Marionina subterranea</i>)	Corexit 7664	
	Finasol OSR-2	>1000
	Finasol OSR-5	
Intertidal limpet (<i>Patella vulgata</i>)	BP1100X	3700 (approx.)
	BP1100WD	270 (approx.)
Crustaceans		
Amphipods (<i>Gammarus</i> spp.)	water-based dispersants ^b	>10000
	petroleum-based dispersants ^c	200 ± 130
Mysids (<i>Neomysis</i> sp.)	water-based dispersants	>4500
	petroleum-based dispersants	~150
Amphipod (<i>Gammarus oceanicus</i>)	AP oil dispersant	10-100 (1.5 days)
Brown shrimp (<i>Crangon crangon</i>)	10 conventional dispersants	3300->10000 (2 days)
	7 concentrated dispersants (unnamed)	2800->10000 (2 days)
Grass shrimp (<i>Palaemonetes pugio</i>)	Corexit 7664	>10 ⁴ (27°C), nontoxic (17°C)
	Atlantic-Pacific	1000 (27°C), 1800 (17°C)
	Gold Crew	150 (27°C), 380 (17°C)
	Nokomis-3	140 (27°C), 250 (17°C)
Fish		
Fish larvae (<i>Pleuronectes platessa</i> , <i>Solea solea</i>)	Corexit 7664	400
Gobies (<i>Chasmichthys</i> , <i>Luciogobius</i>)	Shell dispersant LT	440-480
Stickleback (<i>Gasterosteus aculeatus</i>)	water-based dispersants	950 ± 250
	petroleum-based dispersants	>10000
Dace (<i>Phoxinus phoxinus</i>)	water-based dispersants	1400 ± 200
Coho salmon (<i>Oncorhynchus kisutch</i>)	BP1100X	1700
Killifish (adult)	AP oil dispersant	approx. 100 (2 days),
(<i>Fundulus heteroclitus</i>)	(GFC Chemical Co.)	50-100 (3 days)

^aUnless otherwise noted.

^bExamples of water-based dispersants are Corexit 7664, Cold Clean 500, and Finasol OSR-7.

^cExamples of petroleum-based dispersants are Corexit 8667, Corexit 9550, and BP-1100x.

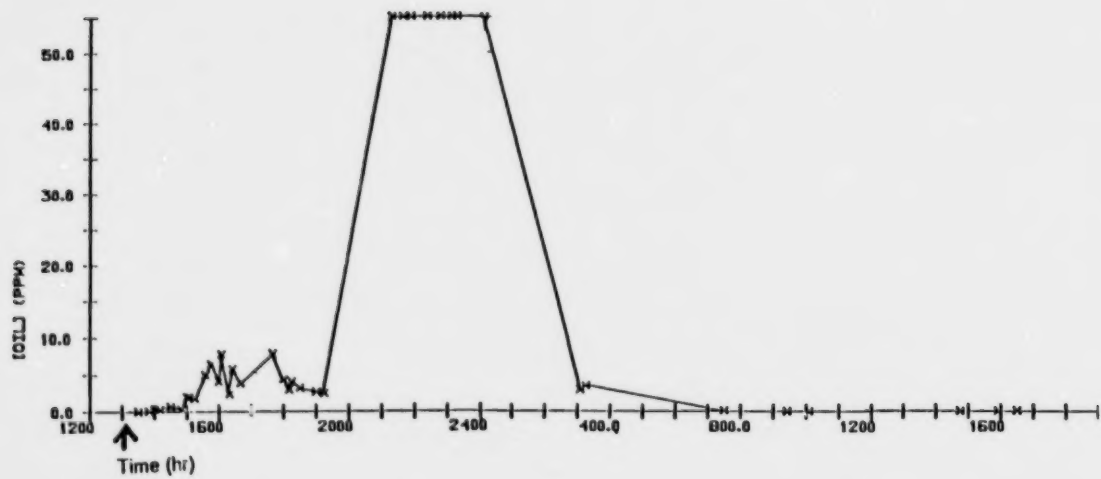


Figure 3. Concentrations of dispersed oil measured at a point approximately 120 m from the diffuser pipe (8 m of depth) before, during, and after the BIOS dispersed oil release. The release started at 1300 hours (arrow) and continued for 6 hours. Because the oil was premixed with dispersant and released at depth under a pycnocline, the oil traveled as a "slug" through the system. Even so, the rate of horizontal diffusion was sufficient to reduce the concentration of dispersed oil to 0.03-0.05 ppm throughout the system by 20 hours after the initiation of the release (Green et al., 1982).

- d. tidal flats
- e. marshes
- f. shallow subtidal areas
- g. low energy bays and harbors
- h. rocky intertidal areas;
- e) aquaculture and commercial areas which are shallow enough to allow impacts from oil spills; and
- f) recreational and industrial areas.

Zone 1 areas are characterized by water conditions (depth, distance, and currents) that will allow dispersed oil to be rapidly diluted to low concentrations, and are far enough away from sensitive resources that dispersant operations would not cause disturbances. In this zone there is a significant likelihood that spilled oil will impact sensitive resources, and an immediate response is required in order to mitigate environmental consequences.

Zone 2

The use of dispersants is conditional in Zone 2 in order to protect sensitive wildlife and other resources. The Federal OSC is required to consult with the RRT and obtain approval of EPA and the State of Alaska prior to the use of dispersants in Zone 2. A spill in Zone 2 must be continuously monitored and the need for dispersant response actions reappraised accordingly.

Zone 2 areas are characterized by water conditions (depth, distance, and currents) that will allow rapid dilution of dispersed oil to low concentrations, a sufficient distance from sensitive resources that an immediate response is not necessary and dispersant operations would not cause disturbances.

Zone 3

The use of dispersants is not recommended in Zone 3. Dispersants may be used in Zone 3 if, on a case-by-case basis, it is determined that the disturbance of the organisms and/or direct exposure to dispersants or dispersed oil would be less deleterious than the impact of spilled oil. As in Zone 2, the OSC is required to consult with the RRT and obtain approval of EPA and the State of Alaska prior to the use of dispersants in Zone 3.

Zone 3 is defined as the area immediately in or around the resources requiring protection, including the resources themselves. Dispersant use in this area may disturb resources, may not have adequate time for effectiveness, may directly expose the resources to dispersants, or may expose other resources to unacceptably high levels of dispersed oil. Examples of these resources are provided below:

- a) endangered or threatened species protected by Federal and State governments;
- b) nesting, spawning, breeding, and nursery areas for mammals, birds, fish, and shellfish;
- c) fish and wildlife concentration areas where these animals feed or rest;
- d) sensitive marine habitats, including:
 - a. seagrass beds
 - b. kelp beds
 - c. shellfish beds
 - d. tidal flats
 - e. marshes
 - f. shallow subtidal areas
 - g. low energy bays and harbors
 - h. rocky intertidal areas;
- e) aquaculture and commercial areas which are shallow enough to allow impacts from oil spills; and
- f) recreational and industrial areas.

SPECIFIC GUIDELINES FOR THE USE OF DISPERSANTS IN COOK INLET

The specific dispersant use zones developed for Cook Inlet are illustrated on nautical charts (Appendix B) and the general rationale for defining these zones is presented below. Because of the seasonal presence of large numbers of commercially valuable adult salmon, that section of Cook Inlet north of a line drawn along the latitude at Anchor Point north of Kachemak Bay is considered to be Zone 3 during the period from July 1 to August 15.

Upper Cook Inlet (North of Point Possession and North Foreland)

Upper Cook Inlet is unique because the extreme upper portion contains two Zone 3 designations (dispersant use not recommended) which are based upon tidal stages. During the first three hours of an ebb tide, the Zone 3 boundary is roughly defined by the five-fathom isobath. For periods outside this time window, Zone 3 is defined as the area north of a line between Point Possession and North Foreland.

A dual Zone 3 designation is needed because dispersant use during a flood tide could result in relatively high concentrations of dispersed oil impacting shallow waters or intertidal habitats. Restricting dispersant use in this area to the ebb tide period eliminates these concerns while still allowing dispersant use in the northern portion of Upper Cook Inlet. Providing the option for dispersant use in this area is deemed desirable due to:

- 1) the high spill potential;
- 2) the difficulty in mechanically containing spills;
- 3) the extreme tidal fluctuations which rapidly transport spilled oil; and
- 4) sensitive coastal habitats requiring protection from potential oil contamination.

Zone 3 - Ebb Tide

The Ebb Tide Zone 3, which exists only during the first three hours of an ebb tide, occurs shoreward of the five-fathom isobath. The five-fathom isobath is used because: 1) the ebb tide will rapidly transport the dispersed oil to deeper waters; 2) benthic communities in Upper Cook Inlet exhibit relatively low productivity; and 3) increased water depths from the high tide stage will enhance dilution capabilities.

Zone 1 - Ebb Tide

The Ebb Tide Zone 1, which exists only during the first three hours of an ebb tide, extends outward from the five-fathom isobath. Dispersant use is restricted to an ebb tide period to prevent high concentrations of dispersed oil from being transported to shallow nearshore waters.

Zone 3 - Flood Tide

The Flood Tide Zone 3 is defined as the area north of a line extending from Point Possession to the North Forelands, for all periods outside of the first three hours of an ebb tide. This designation is necessary due to the potential for strong tidal currents to rapidly transport high concentrations of dispersed oil into important shoreline habitats.

Middle Cook Inlet - South of a Line Between Point Possession and North Foreland to East Foreland and West Foreland

Zone 3

Zone 3 occurs inshore of the five-fathom isobath near the northeast shoreline of this section. The five-fathom isobath is used in this area due to a lack of fish and wildlife resources and the presence of strong currents that run parallel to the shoreline. The Zone 3 designation extends out to

the 10-fathom isobath along the southeast shoreline to provide protection to the Swanson River estuary area. Along the west shoreline, the Zone 3 boundary follows the 10-fathom isobath.

Zone 1

The remaining waters within this Inlet section are designated as Zone 1. This designation will allow for an immediate dispersant use decision to protect important fish and wildlife resources in Cook Inlet.

Lower Cook Inlet - South of East and West Forelands

Zone 3

Zone 3 occurs inshore of the 10-fathom isobath. The 10-fathom isobath provides ample protection to the razor clam beaches and several river estuaries along the east and west shorelines, including Redoubt Bay where large numbers of birds seasonally reside. Around Kalgin Island, a Zone 3 designation is established along the five-fathom isobath due to strong currents that run parallel to the shoreline and the two to five mile buffer provided by the five-fathom isobath. Kachemak and Kamishak Bays are given special protection through an expanded Zone 3 area, due to the important fishery resources associated with these bays. The shoreline in the extreme southern portions of Cook Inlet drops off rapidly resulting in the 10-fathom isobath being located very near the shoreline. Consequently, Zone 3 is defined as an area extending one mile out from the shoreline for areas exhibiting such shoreline characteristics. The one mile buffer distance will allow for dilution of dispersed oil prior to impacting the shoreline or shallow water areas.

Zone 1

Zone 1 is identified as an approximately five-mile wide buffer area extending outside of Zone 3. It is believed that the five-mile wide Zone 1 area will provide adequate time to conduct a dispersant response prior to oil entering the sensitive Zone 3 area.

Zone 2

The remaining waters within this section of Cook Inlet are designated as Zone 2.

Appendix A. DISPERSANT USE FORM COMPILATION OF DATA (modified Pavia and Smith, 1984)

This form will be used by the OSC in deciding whether or not to use dispersants in Zone 1, or to request the use of dispersants in Zones 2 or 3. If dispersants are used, the information requested on this form will be forwarded to the RRT chairman and EPA and state representatives.

1. Spill Data

- a. Circumstances (fire, grounding, collision, etc.)
- b. Time/date of incident
- c. Location of spill (latitude, longitude, river mile, etc.)
- d. Volume of product released
- e. Total potential of release
- f. Type of release (instantaneous, continuous, intermittent, etc.)

2. Characteristics of the Spilled Oil
 - a. Specific gravity
 - b. Viscosity
 - c. Pour point
 - d. Volatility/flash point
 - e. Relative toxicity
3. Weather and Water Condition/Forecasts
 - a. Air temperature, wind speed, and direction
 - b. Tide and current information
 - c. Sea conditions
 - d. Water temperature and salinity
 - e. Water depth and depth of the mixed layer
4. Oil Trajectory Information
 - a. 48-hour surface oil trajectory forecast
 1. Surface area of slick
 2. Expected areas of landfall
 - b. 48-hour dispersed oil trajectory forecast
 1. Oil movement in water column
 2. Surface oil movement and expected landfall
5. Characteristics of Available Dispersants and Application Equipment
 - a. Characteristics of the dispersants:

Product One

Product Two

Product Three

1. name
2. manufacturer
3. when available
4. location(s)
5. amount available
6. type of containers
7. characteristics
 - a. toxicity
 - b. reactions
 - c. applicability to spilled oil
 - d. other
8. application methods
9. miscellaneous

- b. Type of transportation and dispersing equipment

Company One

Company Two

Company Three

1. name
2. location
3. time to arrive
4. equipment available
5. other

6. Information about Available Dispersant and Dispersing Equipment
 - a. Name of the proposed dispersant on EPA acceptance list
 - b. Type (self-mix, concentrate, etc.)
 - c. Proposed application methods and rates

- d. Efficiency under existing conditions (percent dispersed and volume dispersed)
- e. Schedule of the dispersant operation
- f. Location of the area to be treated
- g. Surface area of the slick which can be treated in the scheduled time period

7. Conventional Methods and Time Considerations for Containment and Cleanup Feasible and Available.

	<u>Dispersant-treated spill</u>	<u>Untreated spill</u>
a. Containment at the source		
b. Shoreline protection strategies		
c. Shoreline cleanup strategies		
d. Time necessary to execute response		

8. Habitats and Resources at Risk

	<u>Dispersant-treated spill</u>	<u>Untreated spill</u>
a. Shoreline habitat type and area of impact		
1.		
2.		
3.		
4.		
b. Resources*		
1. Endangered/threatened species		
2. Marine mammals (pupping, migration)		
3. Waterfowl use (nesting, migration)		
4. Shellfish (spawning, harvesting)		
5. Finfish (spawning, release migration, harvest)		
6. Commercial use (aquaculture, water intakes, etc.)		
7. Public use areas (parks, marinas, etc.)		
8. Other resources of special significance		

*indicates seasonal considerations

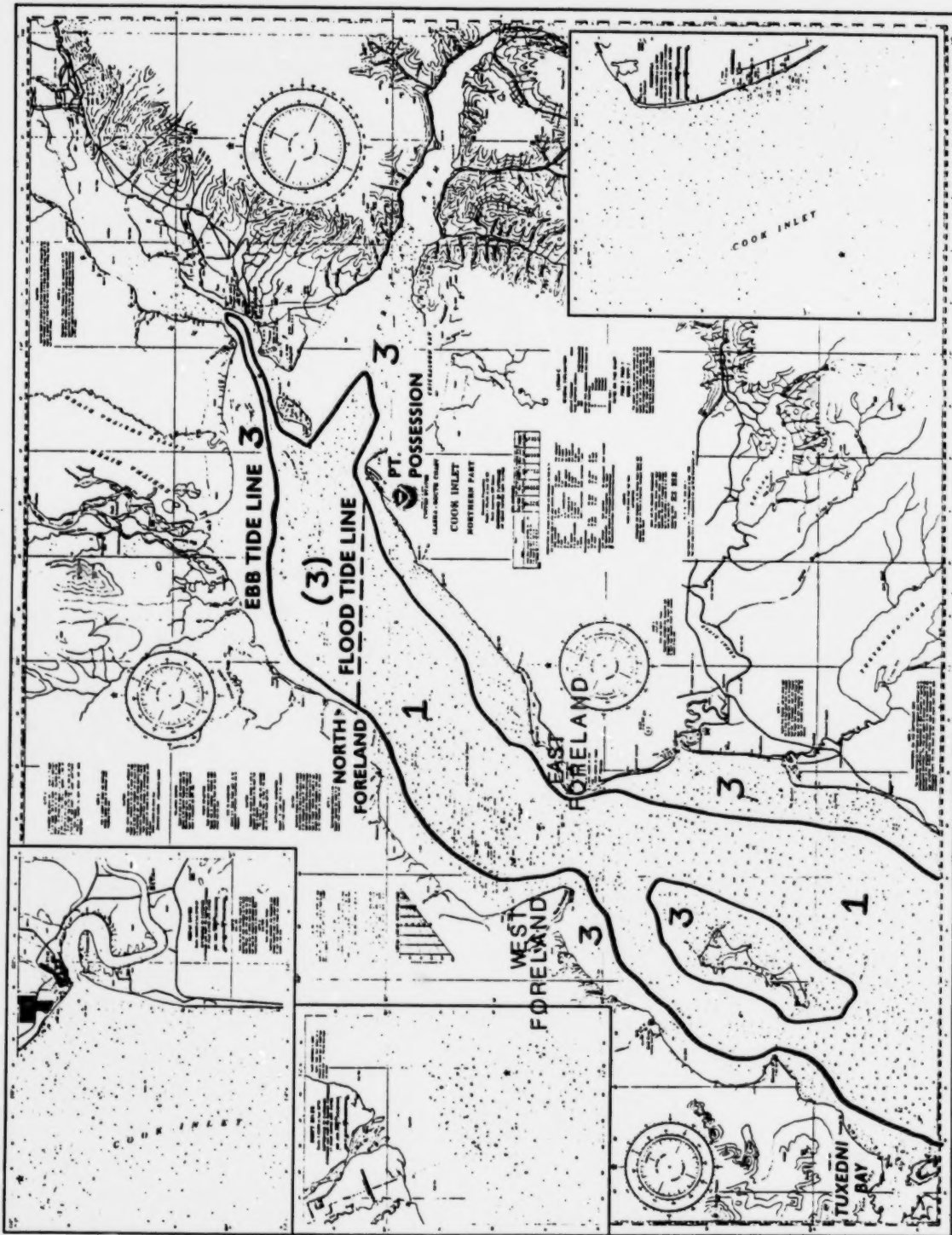
9. OSC's Evaluation of the Consequences of a Dispersant Application Decision

- a. Will application of dispersant remove a significant amount of the slick from surface water?
- b. Can dispersants alter the extent or location of shoreline impacts?

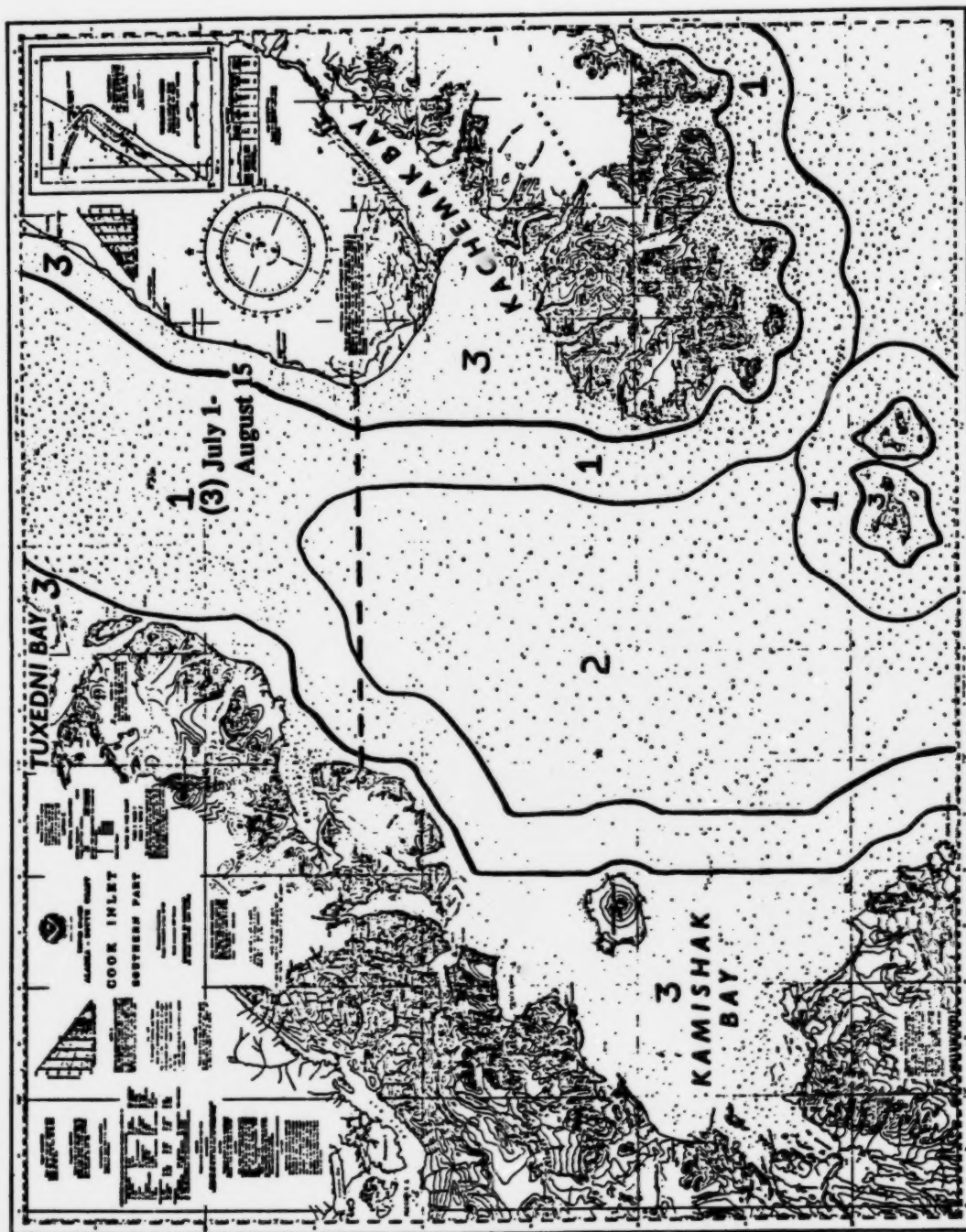
- c. Can the damage to endangered or threatened species, marine mammals, and waterfowl be lessened?
 - d. Will the damage to habitats and resources resulting from chemical dispersion be less than those resulting without chemical dispersion?
 - e. If recreational, economic, and aesthetic considerations are a higher priority than natural resources, what is the most effective means of their protection?
10. Economic Considerations
- a. Cost of the dispersant operation
 - b. Cost of conventional containment and protection
 - 1. with dispersant use
 - 2. without dispersant use
 - c. Cost of shoreline cleanup (cost per barrel x number of barrels reaching shoreline)
 - 1. with dispersant use
 - 2. without dispersant use
11. OSC Decision for Zone 1/Recommendation to the RRT for Zones 2 and 3
- a. Do not use dispersants
 - b. Use dispersants on a trial basis to ensure effectiveness
 - c. Disperse in limited or selected areas
 - d. Disperse to the maximum extent possible with accepted methods
12. RRT Evaluation of the Consequences of a Dispersant Application Decision (for Zones 2 and 3)
- a. Will application of dispersant remove a significant amount of the slick from surface water?
 - b. Can dispersants alter the extent or location of shoreline impacts?
 - c. Can the damage to endangered or threatened species, marine mammals, and waterfowl be lessened?
 - d. Will the damage to habitats and resources resulting from chemical dispersion be less than those resulting without chemical dispersion?
 - e. If recreational, economic, and aesthetic considerations are a higher priority than natural resources, what is the most effective means of their protection?

Appendix B. DISPERSANT USE ZONES, WITH ENLARGEMENTS OF ANCHORAGE, DRIFT RIVER, AND EAST FORELANDS.

DISPERSANT USE ZONES

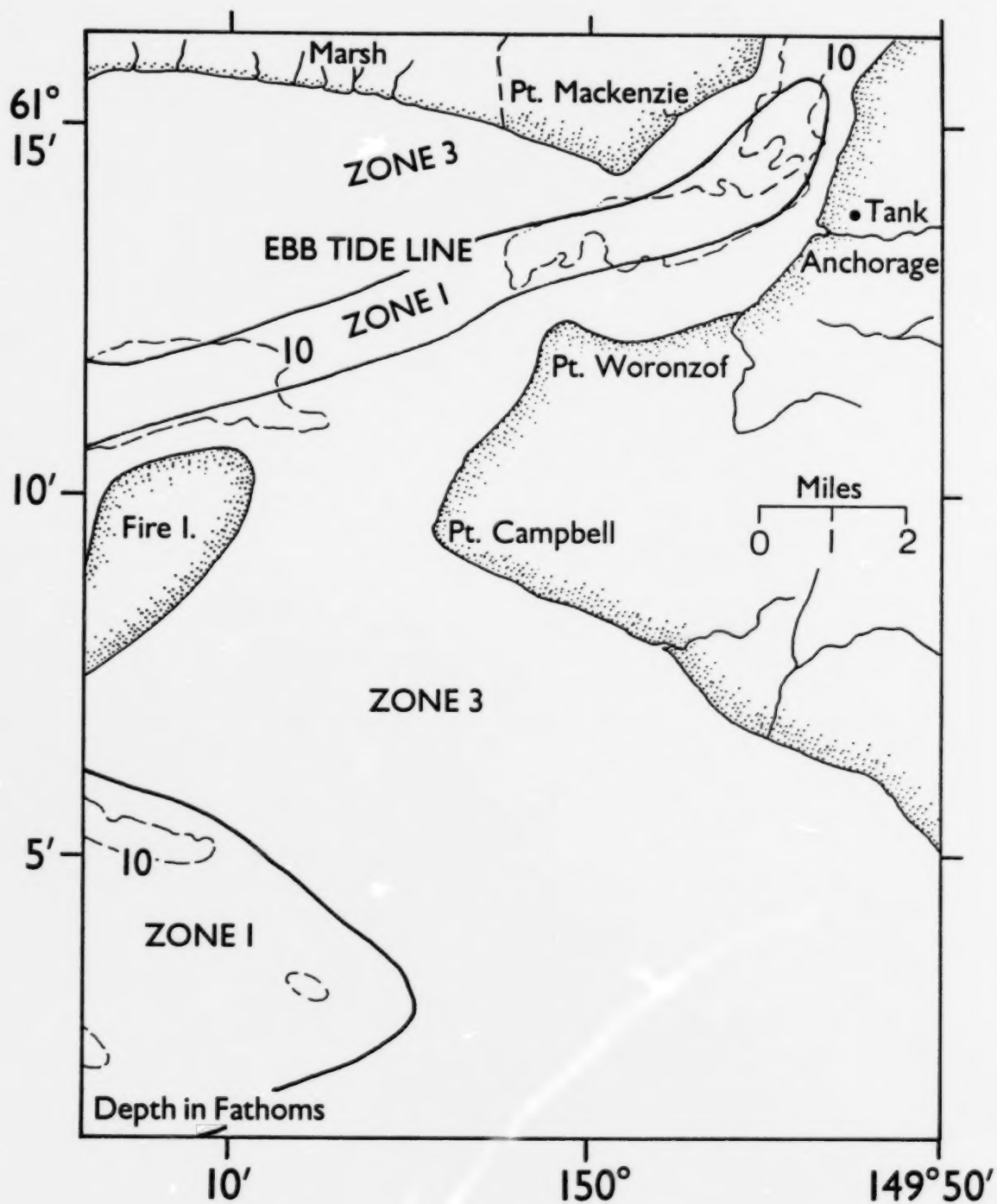


DISPERSANT USE ZONES

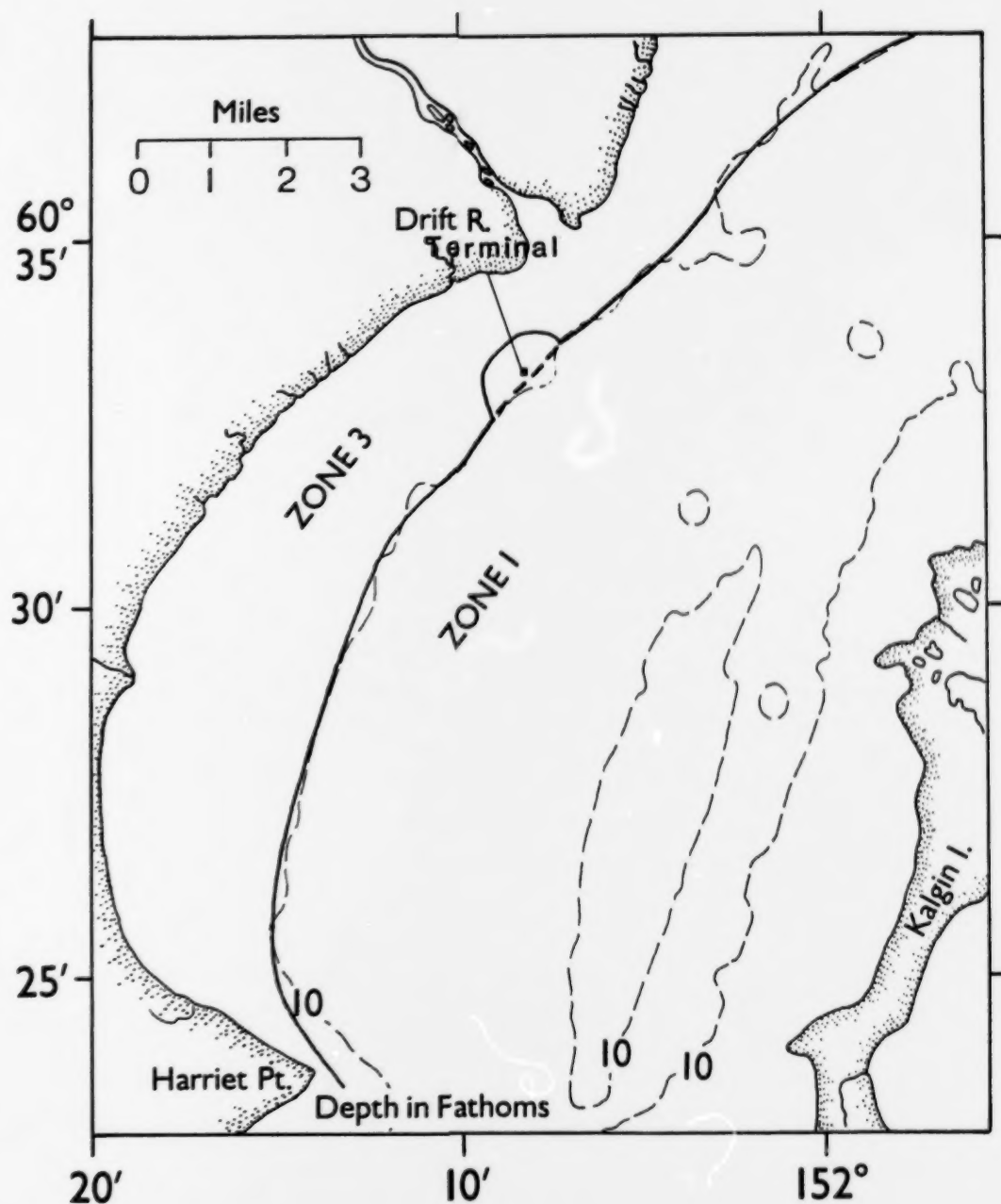


Cook Inlet north of the dotted line is considered Zone 3 from July 1 to August 15

Anchorage Dispersant Use Zone Enlargement

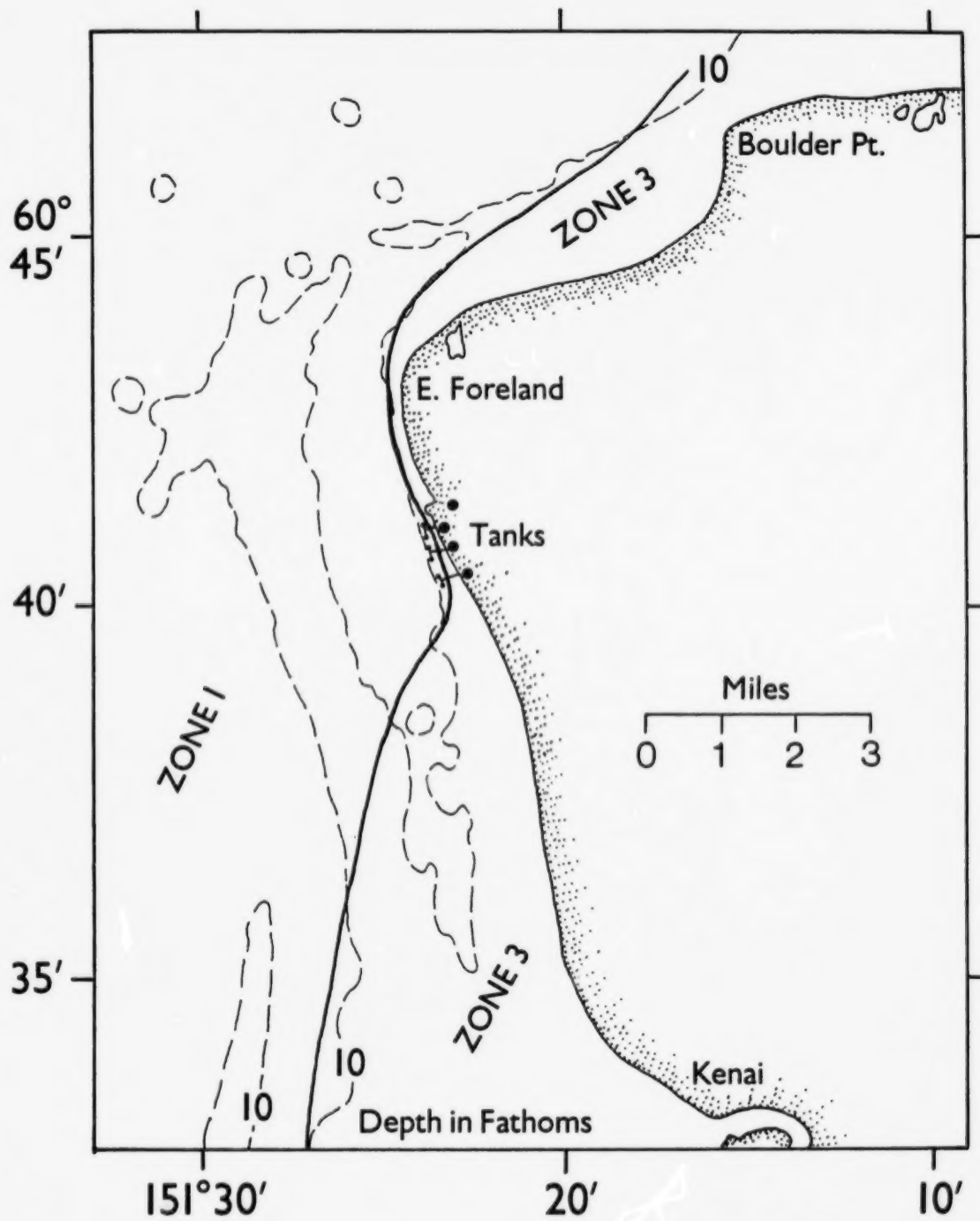


Drift River Dispersant Use Zone Enlargement



ZONE 1 EXTENDS 1/2 MILE AROUND TERMINAL ON SLACK BEFORE EBB TO MAX EBB. AT ALL OTHER TIMES ZONE 1 EXTENDS ONLY TO DOTTED LINE EAST OF TERMINAL.

East Foreland Dispersant Use Zone Enlargement



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FRESHWATER OILSPILL RESEARCH PROGRAM-
FIELD TRIAL

by

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1.0 BACKGROUND

The Freshwater Oil Spill Research Program (FOSRP) Field Trial was conducted in the Perryvale region of Alberta during the period July 12 - 16, 1985. This trial represented the culmination of four years of effort by the FOSRP Committee, and the first time that the effects of a dispersant-treated oilspill have been studied in a natural, freshwater environment.

The project was coordinated by Esso Resources Canada Limited, with funding and logistic support provided by PACE (Petroleum Association for the Conservation of the Environment), PROSCARAC (Prairie Region Oil Spill Containment and Recovery Advisory Committee) and Esso.

Research expertise was contributed by Esso Resources, the Energy Resources Conservation Board, the Environmental Protection Service, and the University of Alberta Departments of Botany, Zoology and Microbiology. Advice and review was provided by Alberta Fish and Wildlife, Alberta Environment, and Alberta Energy and Natural Resources. On-site laboratory facilities and personnel accommodation was provided by the University of Alberta Meanook Biological Station.

2.0 EXPERIMENTAL PROGRAM

The experimental program took place approximately 125km north of Edmonton, Alberta, in the Athabaska region of Alberta. The study area comprised three waterbodies, which ranged in size from 10 to 19 hectares. Maximum depths were approximately 1.5 metres.

2.1 Experimental Overview

The overall purpose of the FOSRP program was to test the ability of dispersants to mitigate negative environmental effects resulting from oilspills in a freshwater ecosystem. Based on the results of experiments conducted over the preceeding three years under the FOSRP program, Corexit 9550 was established as the dispersant of choice. This dispersant was developed for cold-water and or low-salinity water, and was shown to be less toxic to aquatic organisms than other dispersants designed for similar application.

The dispersant was applied in a 1:10 (dispersant: oil) ratio to a 3 m³ oilslick of fresh Norman Wells Crude, on the "West" slough. Two other waterbodies were used as controls. One, the "South" slough received a treatment of 3 m³ of oil, with no dispersant; the other, the "East" slough received neither oil nor dispersant.

Various ecological components of each waterbody were monitored, and results compared. Components studied included limnological (physical/chemical), botanical (shoreline and aquatic), microbial, and planktonic.

Prior to the field program, techniques were developed to pump oil onto the surface of the waterbodies, to retrieve water samples from beneath the oil slicks, (Swiss and Gill, 1984) and to spray dispersant from a helicopter using agricultural crop-spraying equipment. In addition, an aircraft-mounted, remote-sensing package to track oilslicks was used (Goodman et al, 1986).

2.2 Regulatory Compliance/Permits

Prior to the field trial, several government approvals were required, including Letters of Authority from the Public Lands Disposition Branch and the Water Quality Branch of Alberta Environment, and the Public Lands Division, Alberta Energy and Natural Resources. In addition, an inventory for waterfowl utilizing the study area was conducted, and a Wildlife Damage Permit was obtained from the Fish and Wildlife Division.

Permission was granted by the Director of Standards and Approvals to conduct the field trial, subject to a number of terms and conditions. Representative water samples were obtained from study area sloughs according to a pre-arranged schedule and methodology.

2.3 Spill Containment

A fully-equipped Oil Spill Containment and Recovery (OSCAR) trailer was on-site to ensure immediate response capability was available, should weather conditions or an inadvertant mishap result in temporary loss of control of the oil during the exercise. As part of ensuring control, radio phones were in place to give immediate access to government agencies should the need arise.

3.0 METHODS AND RESULTS

Materials, methods and results are discussed under the headings listed below. Conclusions and some interpretation of data are included where available.

3.1 Oil and Oiling of Experimental Sites

The oil used for both West and South Sloughs was unweathered Norman Wells Crude. Hoses were laid at each site, running 525 m and 200 m respectively to the west and south sites. Discharge ends of the hoses were wired onto plywood/styrofoam spill-plates positioned approximately 50 m offshore at each site.

Initial plans to begin the field exercise on July 11 were postponed due to unstable weather conditions. Spills subsequently took place July 12.

3.2 Dispersant Application

Pre-spill testing of the dispersant application system was conducted using a Bell 47 helicopter, equipped with two side-mounted tanks and an extendable spray boom was used for the tests.

From the pre-testing, it was determined that a suitable spray could be applied at the preferred 1:10 (dispersant:oil) application ratio by the helicopter flying 40 km/h at 15 m altitude, using a 7.6 m boom equipped with size D10 nozzles and size 45 cores. Droplet sizes within the dispersant spray were measured by placing Kromecoat cards on sampling platforms within the oil slick prior to dispersant application. Three hundred litres of dispersant were used. To facilitate direct observation of the aerial spraying, 18 grams of rhodamine dye was added to the dispersant.

Oil at the west site was left to spread for approximately one half hour (08:54 - 09:26 hrs), after which the helicopter flew successive passes over the slick to apply dispersant. Spraying of the entire slick was completed within 10 minutes (09:36 hrs). A distinct demarcation line enabled the pilot to accurately position the helicopter for successive passes, with a minimum of overspray.

Once spraying of the slick was complete, a single over-flight was made of a marked strip of vegetation along the southwest shore of the slough. This vegetation plot was established to measure any effects the dispersant may have had on shoreline plant species.

Visual inspection of the Kromecoat cards placed on the sampling stations confirmed that the dispersant was applied in an even pattern, and at a drop size consistent with the needs of the program. Precise droplet size will be determined at a later date, using the Kromecoat card information.

3.3 Meteorology

A meteorological trailer, equipped to measure wind speed and direction, air temperature, and barometric pressure was positioned within 200 m of the West slough. Data were collected to define prevailing local conditions (pre-spill), as well as to document meteorological conditions during the spill and immediate post-spill periods. During the pre-spill period, frequent weather

forecasts were obtained from Environment Canada, to ensure the spill exercise would not be initiated when inclement weather was predicted in the area.

During spill day, the prevailing wind at West Slough was westerly, ranging in speed from 0 to 28 km/h. During the critical spill period (08:45 - 10:00 hrs), wind velocities were westerly at 2 - 18 km/h.

Based on direct observation, winds at West Slough were more variable than those recorded at the meteorological trailer, 200 m away. However, overall, winds were generally westerly; a fact confirmed by the slick drifting eastward after the spill was completed.

During spill day, air temperature ranged from an early morning minimum of 11°C, to a mid-day maximum of 26°C. During the oil-spill/dispersant application period, temperatures averaged 18°C.

3.4 Remote Sensing

An aircraft-mounted, remote-sensing system was used to record the shape, position, and areal extent of the two oil slicks. This remote sensing package was comprised of three cameras, a video cassette recorder, and a computer-based processing system, mounted in a twin-engine Cessna 411 aircraft.

Missions were flown over both the oil-control slough and the slough which had oil and dispersant applied. The remote sensing flights were initiated before the spill and continued for about two hours after the spill. Another remote sensing flight was undertaken three days after the spill.

Initial computation of slick size was done onboard the survey aircraft. An examination of the infrared video imagery clearly shows the application of the dispersant Corexit 9550 reduced the volume and area of the thick oil. However, due to the interfering effects from land objects and sun glitter, difficulties have been encountered in automatically processing the collected data.

3.5 Physical/Chemical Study Program

Several physical/chemical tests were conducted on water samples obtained from west and south sloughs. These tests included measurement of oil concentration in the water column, oil weathering, oil-slick thickness, and oil/dispersant droplet size.

3.5.1 Water Sampling

A sampling system developed by Esso was used to collect water samples for Microtox Tests and 96 Hour Static Fish Tests, plankton studies, and measurements of particle size and oil concentration in the water column.

Two sampling trees, with ports at 25 cm and 50 cm subsurface, were deployed at each of the South and West sloughs. Prior to the spill, sampling trees were placed approximately 50 m offshore, 10 m apart in the two areas where, given prevailing winds, the slicks were anticipated to drift. A 4-inch rope boom was used at each site to hold a portion of the slick in position over the sampling sites.

This system provided the convenience of a stable, shore-based sampling station, while at the same time avoiding unnecessary and disruptive boat traffic through the slicks.

3.5.2 Oil Concentration in Water Column

The concentration of oil in the water column beneath the oil slick was measured by fluorescence. At the West Slough, where dispersant was applied to the oil slick, the flow-through fluorometer was connected directly to one of the 25-cm depth sampling ports. The three remaining sample streams on the West Slough, and all four sample streams on the South Slough, were collected in one litre bottles at regular intervals for later analysis. To ensure complete data collection, grab samples were taken as backup to the fluorometry data.

Measurements of oil concentration as a function of time after the oil was spilled, are presented in Figures 1-4. Figure 1 shows the oil concentration 25 cm below the surface of the West Slough near or under the slick after it

was sprayed with Corexit 9550 dispersant. The oil concentration rose gradually as wave action circulated the oil droplets into the water column, peaking after about 5 hours at 0.8 PPM. Note that the flow through fluorometer was off scale at this point and 0.8 PPM value was measured later on a grab sample. At about 9 hours after dispersant application another peak in concentration occurs, but at all times the amount of oil in the water column remained low. This was undoubtedly due to the very low wave energy encountered in such a small body of water and to the fact that Corexit 9550 requires more energy than some other dispersants to break oil into circulating droplets (G. Canevari, personal communications).

In a recent test of Corexit 9550 conducted at the Esso wave basin facility in Calgary, the oil concentrations, shown in Figure 2, were obtained at 50 cm depth below the water surface. Regular non-breaking waves 20 cm high with a 1.6 second period were used in this experiment. Concentrations of 2.5 PPM were reached by the end of the test after 3 hours. At the West Slough, winds were variable during the test, but generally from the prevailing direction (W to NW) at a speed of 10 to 15 km/hour. Given the short length (fetch) of open water and the presence of forest around much of the slough, such winds would not generate waves of the size or frequency used in the wave basin test. With lower wave energy one would expect less circulation of oil into the water column. Compared to the wave basin tests this is what is observed in the West Slough during the first three hours of the test.

Figures 3 and 4 show the oil concentrations measured from the grab samples at the West and South Sloughs. These samples were extracted with CH_2Cl_2 and then measured by fluorescence spectrometry. Although the number of data points is relatively sparse compared to the flow-through fluorometer system (1 data point/sec) some interesting results appear. At Station 1 on the West Slough, 25 cm depth generally agrees with the previous flow-through fluorometer graph except near the end of the test. As expected, the 50 cm depth results are lower. Clearly, more oil circulated beneath Station 2 than Station 1. From seven to nine hours after the oil was spilled, a dramatic increase occurred in the oil concentrations at both the South and West Sloughs. It is not immediately apparent what has caused this result as there was no change in the variable (but low) wind speed or direction at this time. The weather station had been placed in a large clearing northwest of

the West slough and the readings obtained there are thought to be representative of weather in the general vicinity of the sloughs. It does appear, however that a cloud of high oil concentration water moved through the sampling sites of both sloughs at about the same time. It is possible that circulating currents set up by differential heating started at this time. The sloughs are small (approximately 15 hectares) and generally less than one meter deep. During the day, the upper-surface water-layers are warmed by convection currents in the air. Layers lower in the water column are heated more slowly by solar radiation. By late afternoon when the air temperature is dropping, the upper water-layers will begin losing heat faster than deeper water. Circulating currents will result as the upper, cooler water falls. High concentrations of oil suspended in the water column just below the water surface would then be circulated past the sample ports into deeper water.

It is curious that in general there was little difference in concentration values between the dispersed oil and the weathered oil slough. This contradicts visual evidence which clearly suggested less floating oil remained on the dispersed (West) Slough during the test. This may be an artifact of sample station placement in the sloughs. It is clear however, that to obtain an oil material balance, many more sampling stations would be required so that the oil movement in the water column could be followed.

3.5.3 Oil Weathering

In order to obtain an estimate of the amount of oil lost due to evaporation of the slick during the test, a number of 5 ml oil samples were taken from the spill. These were later subjected to simulated distillation by gas chromatography. See Table 1 for evaporation rates of Norman Wells crude oil during the experiment.

3.5.4 Oil Slick Thickness

During the test spills, samples from the two slicks were taken at various times and locations in order to determine the slick thickness. Results obtained from weighing the hydrocarbon extracts indicated the West Slough (dispersed) slick was generally thinner overall than the South Slough slick, although the ranges in slick thickness recorded at each site were similar:

0.001 - 0.4 mm for West Slough; and 0.001 - 0.4 mm for South Slough.

Throughout the west-site monitoring period, slick thickness was relatively constant around 0.001 mm.

South Slough measurements showed slick thickness to be quite variable during the monitoring period, with values generally higher than those recorded at the west site. Visual observations confirmed that the slick on South Slough was heavier than the relatively thin sheen noted at West Slough.

TABLE 1 Initial Boiling Points (IBPs) of Unweathered Norman Wells Crude and Oil Samples Taken at Intervals During the Field Trial

Location	Time	IBP (°C)	% Lost By Weathering
Fresh Norman Wells Crude		18	0
West Slough	10:20	98	9
South Slough	13:05	91	7
	13:45	118	14
	16:00	141	20
	18:10	152	23

3.5.5 Oil/Dispersant Droplet Size

Oil/dispersant droplet size in the water column (West Slough only), was measured taking on-site samples collected from ports connected to the subsurface sampling system. Because the water-sampling system drawing water from the 50 cm port of Station 2 was inoperative during the sampling period, only results from the other three ports can be reported. Before counting the oil/dispersant particles, filter paper was used to remove suspended solids from the water samples. This filtering removed a portion of the oil from the sample, and the results of this data are therefore questionable.

Generally, the data for both the 25cm and 50 cm depth at Station 1 show a large increase in the number of particles at all sizes about one hour after the dispersant was applied. Data from the 25cm depth at Station 2 show this increase about 40 minutes after the dispersant was applied. Two and a half hours later (1200 hrs), there was again an increase in the total number of particles at all sizes at the 25 cm depth, Station 1 (Figure 5). This second increase was not noted at the 25cm depth, Station 2 (Figure 6). However, this dramatic increase was noted at Station 1 , 50 cm, five hours after the dispersant was sprayed at approximately 1500 hrs (Figure 7). Note in Figure 7, eight hours after the dispersant was sprayed there was a second increase in the total number of particles. This is consistent with the fluorometry data and may be attributed to the circulation patterns of the slough set up by differential heating.

3.6 Botanical Study Program

Two components of the botanical community were studied: aquatic vegetation, and shoreline vegetation. Study effort was directed primarily at documenting changes in plant communities, and the degree of necrosis attributable to oil, or oil-plus-dispersant treatments.

Both the South and West Sloughs were mapped in terms of their shoreline vegetation types. Much of the organic material at both sloughs was "peaty". The West Slough supported a moderate growth of phyto-plankton, which in July consisted primarily of blue-green algae. The South Slough had a depth very similar to the west, (1-1.4 m), and a soft bottom consisting primarily of fine

peaty material. The smaller size of the South Slough, and the presence of a mature forest along its borders, provided a degree of protection from winds. Densities of phytoplankton and particulate matter were lower than those observed at the west site.

No extensive damage to the shoreline vegetation was observed immediately after application of the oil and dispersants to the West slough. Some drops of dispersant were noted on the foliage of plants growing along the shoreline. These spots later turned necrotic but damage was sublethal. Other plant species with broad leaves were carefully examined around the shoreline and within the plot sprayed with Corexit 9550. Some traces of the dispersant were observed on the foliage, but the extent of damage was considerably less than that incurred through. Patches of floating oil were noted around portions of the shoreline one week after treatment but not after one month.

Oil damage to shoreline vegetation in the South Slough was also minimal. This site contained numerous floating islands. While the oil killed the vegetation on one island next to the spill site, new growth was observed one month after oiling. Oil that washed ashore coated lower portions of vegetation and caused some mortality, although vegetation on other islands and the remaining shoreline appeared undamaged. A definite surface slick persisted after three months. Wave action washing oil from the vegetation may have contributed to this slick.

Although the short term effects of the crude oil, dispersed oil, and dispersant on the shoreline plant communities were minimal, contamination of the pore waters in and around the shoreline may pose a delayed threat to the vegetation. Ongoing monitoring is being undertaken until effects cannot be detected.

3.7 Microbiological Study Program

The microbiological program consisted of two major experimental components which were designed to monitor the effects of a freshwater oilspill treated with a dispersant (Corexit 9550), and a fertilizer.

The first component monitored microbial communities in sloughs treated with oil, and oil-plus-dispersant. As with other FOSRP field programs, the East Slough served as a "no-treatment" control. Several chemical/physical and

microbiological parameters were studied, including water column bacteria, sediment, and microbial populations and enzyme activities. Other physical/chemical analyses included the following: temperature; dissolved oxygen; pH; conductivity; total organic and inorganic phosphorus; nitrogen counts; in-situ degradation of oil; extraction of vegetation associated hydrocarbons; quantification of oils and greases content of selected samples; and "in-lab" oil degradation potential assessment.

Analyses of labile components were performed immediately at the Meanook Biological Station, while analyses of stable components such as oils and greases were performed later on stored, frozen samples.

To date, the slow-release fertilizer experiments are incomplete and will not be discussed. The results from the other experiments indicate that the oiling of the West and South Sloughs had very little effect on the indigenous bacterial populations. Little change in population numbers was observed, and most changes could be explained in terms of seasonal influences. There appeared to be some enrichment for aromatic hydrocarbon degraders in the oiled sloughs. No major beneficial or deleterious effects of the addition of oil or dispersant were observed in the tests employed.

3.8 Plankton/Toxicity Study Program

Four test programs were conducted to assess the effects of the experimental program on plankton. These programs included the quantification of selected, dominant, planktonic species, determination of plankton biomass, measurement of metabolic rate and evaluation of acute and subacute toxicity.

3.9 Microtox tests

As an adjunct to the tests described above, testing was conducted of the acute toxicity of slough waters, rhodamine-dyed Corexit 9550, and Norman Wells crude oil, using the Microtox system. The information from the microtox system indicates that the oil/dispersant mixture had no significant effect. The slough samples were taken on spill day, and up to four days later.

4.0 SUMMARY AND RECOMMENDATIONS

The following section summarizes the results of the 1985 Freshwater Oilspill Research Program Field Trials.

- All regulatory compliance and requirements for permits were met, and will continued to be met in the post-spill monitoring program.
- The operational application of the dispersant was judged to be very successful.
- The remote sensing component of the field trial provided useful information for the interpretation of dispersant effectiveness.
- The fluorometers monitoring the concentration of oil in the water column recorded low concentrations of oil in both sloughs, and were successful in identifying the recirculation patterns of the west slough.
- The oil/dispersant droplet size measurements showed the chemically treated oil effectively dispersed oil into the water column.
- Both the botanical and microbiological programs indicated that neither the application of dispersant-alone, oil-alone, nor the oil-and-dispersant mixture caused any beneficial or deleterious effects. Similarly, the Microtox system showed there was no significant toxicity of the dispersed oil mixture, or oil-alone on the sloughs.

On the basis of the field trial conducted on the freshwater sloughs, the following recommendations are made:

- To obtain an oil material balance, more sampling stations would be required to ensure oil movement in the water column could be followed.

- To ensure complete coverage of oil movement in the water column at all times, the fluorometers should be connected to each part.
- A method to remove the suspended sediments from the water should be developed prior to determining oil/dispersant droplet size.
- A marker should be included on the remote sensing data collection system to assist in image analysis.

Acknowledgments

The authors would like to acknowledge all the researchers involved in the Freshwater Research Oilspill Program, the government agencies who granted permission for the experiment to take place, the PROSCARAC (Prairie Regional Oil Spill Containment and Recovery Committee) Research and Development Committee of the Canadian Petroleum Association, PACE (Petroleum Association for the Canadian Environment) and Esso Resources Canada Limited for their continued support of the program.

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FIGURE 1

OIL CONCENTRATION AT 25CM DEPTH

WEST SLOUGH

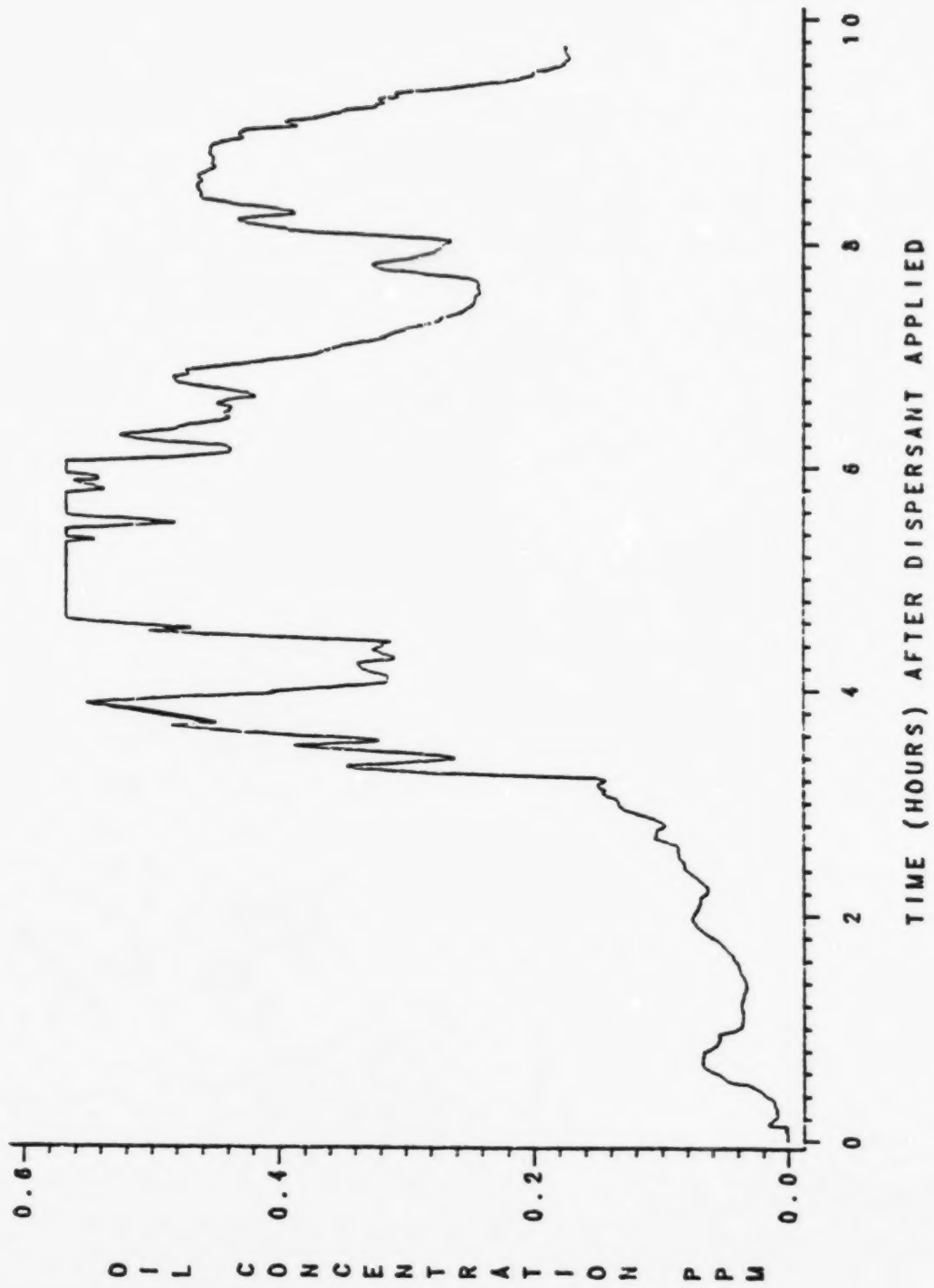
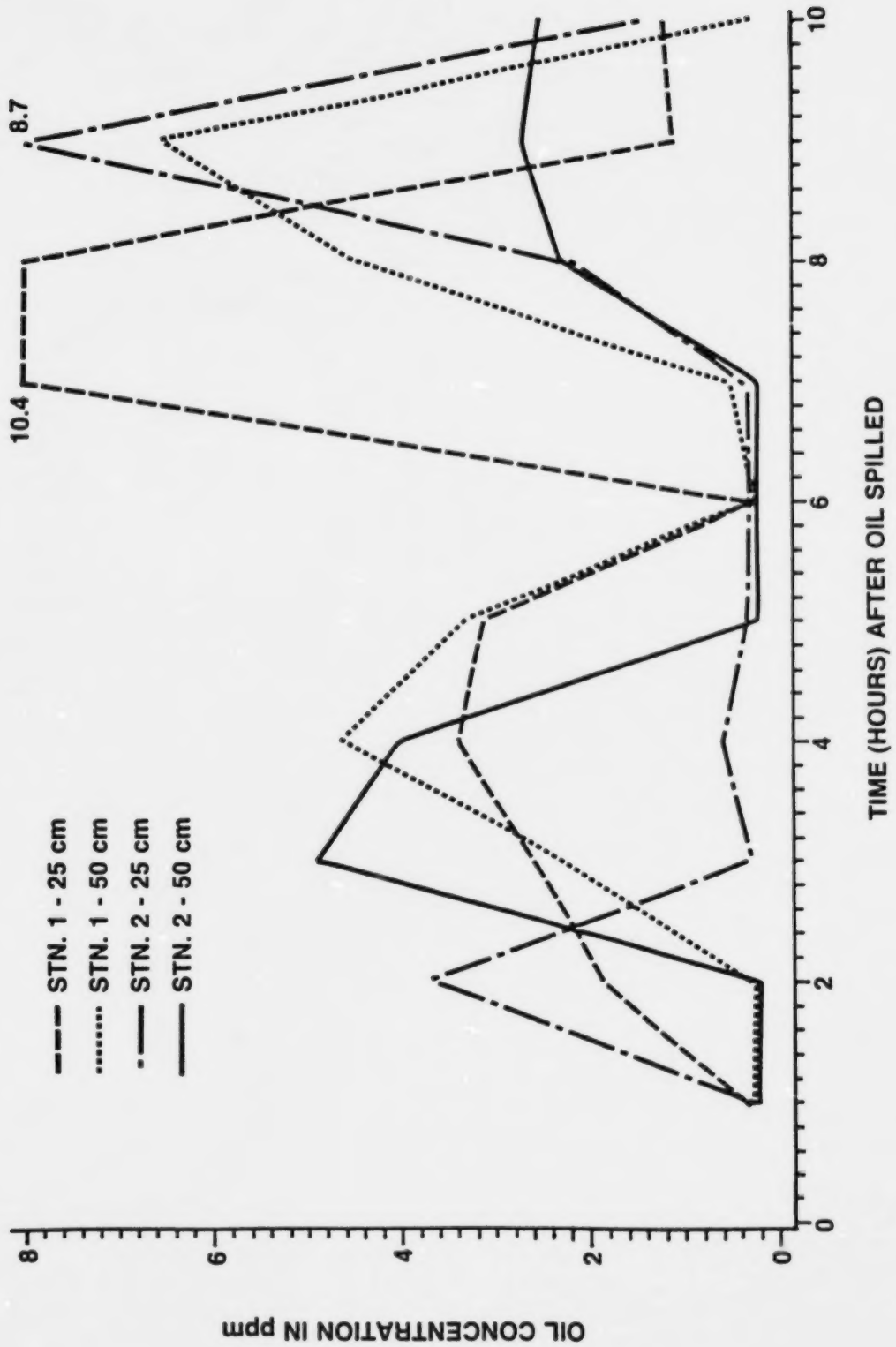


FIGURE 2

BASIN TRIAL - 20CM REGULAR WAVES



FRESH WATER OIL CONCENTRATION SOUTH SLOUGH



FRESH WATER OIL CONCENTRATION WEST SLOUGH

FIGURE 4

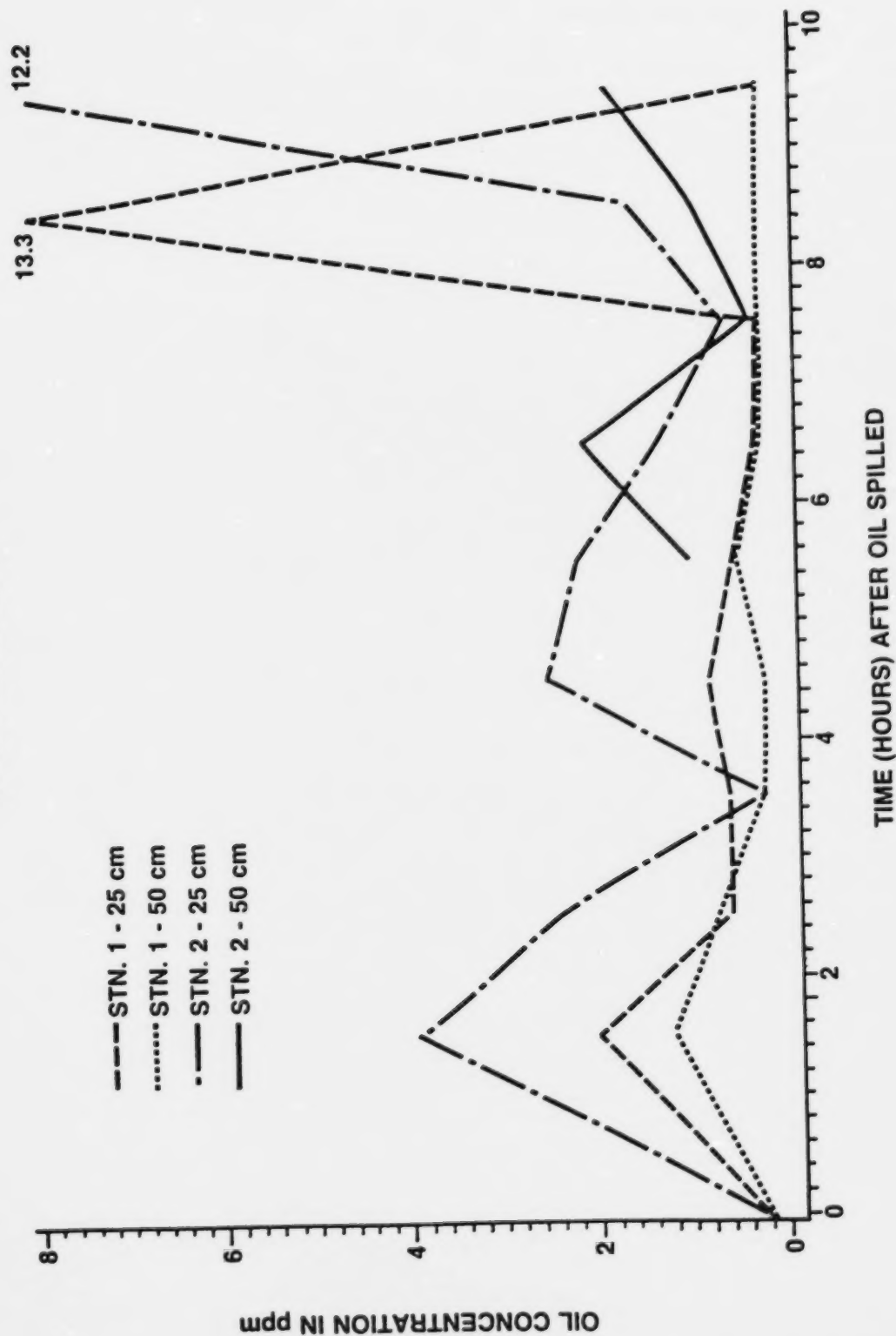
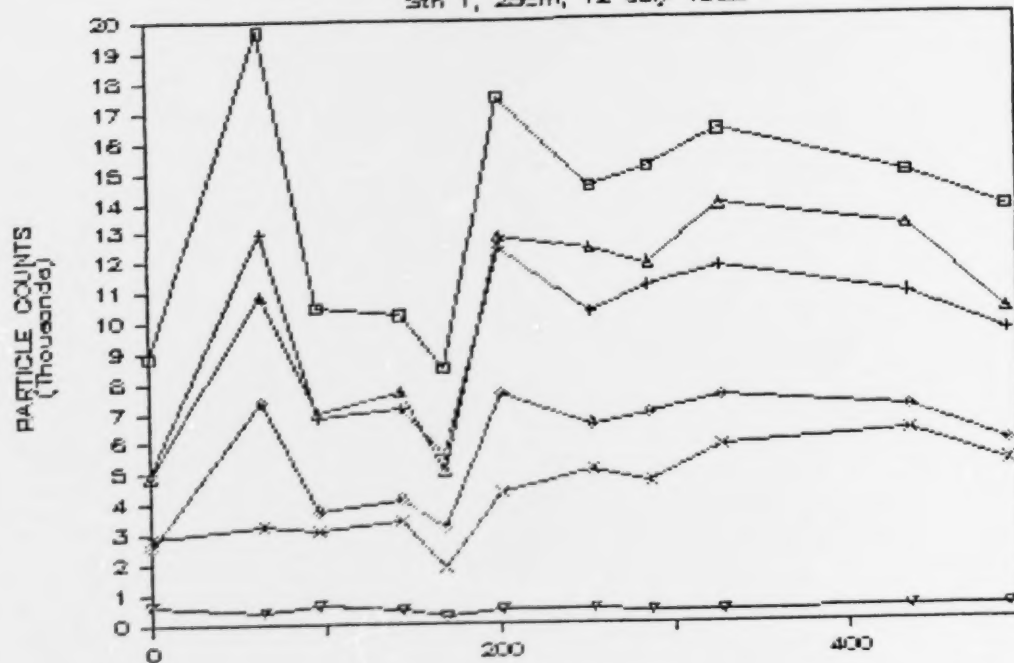


FIGURE 5

MEANOOK FIELD TRIALS

Stn 1, 25cm, 12 July 1965



□ 3.0m

+ 4.0m

● 5.0m

△ 6.0m

X 10.0m

▽ 20.0m

FIGURE 6

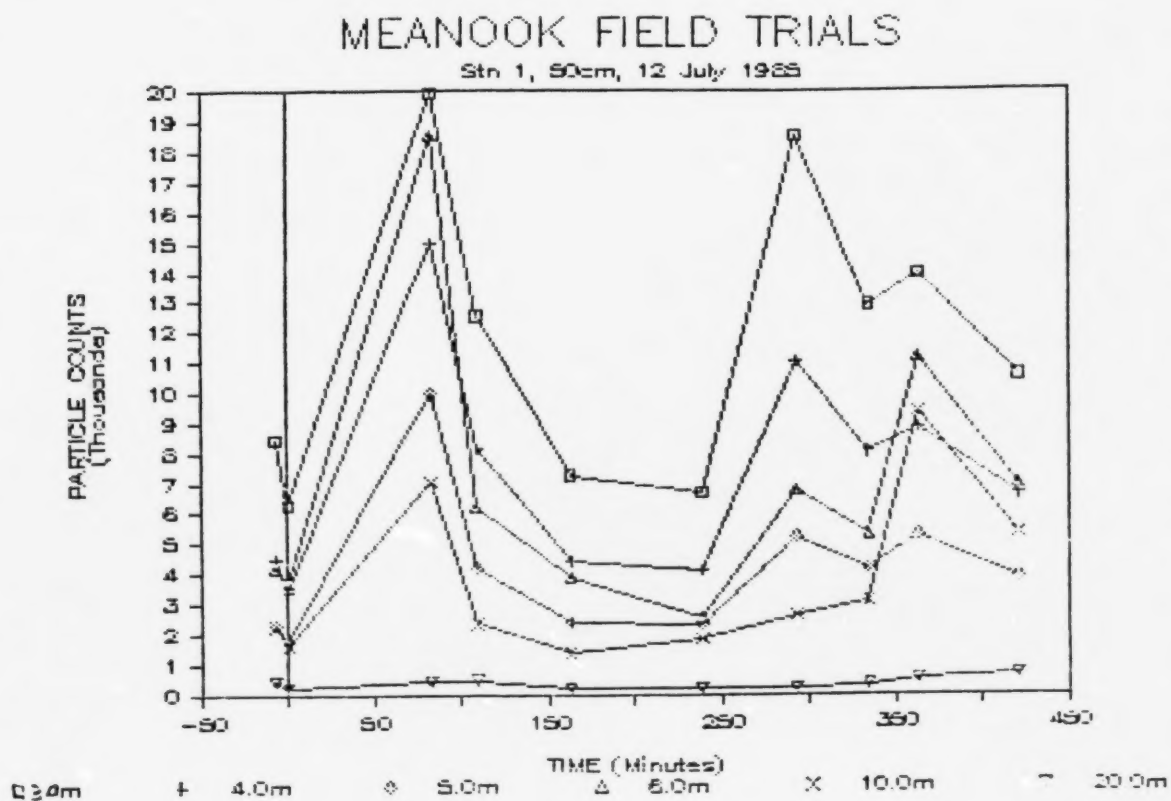
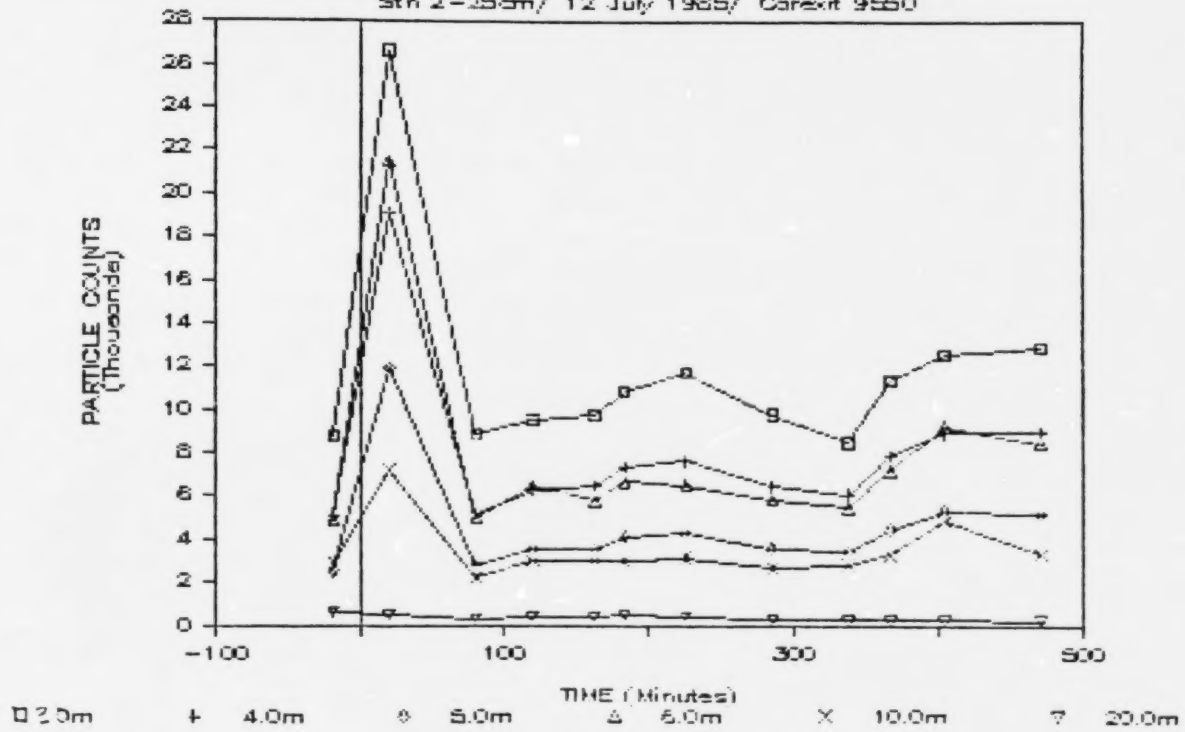


FIGURE 7

MEANOOK FIELD TRIALS

Stn 2-25cm/ 12 July 1985/ Carexit 9550



USE OF REMOTE SENSING DURING THE FRESHWATER DISPERSANT EXPERIMENTS

by

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One of the components of the Freshwater Oil Spill Program Dispersant trial conducted near Athabaska, Alberta, was the use of a simple remote sensing system to detect the oil. Both ultraviolet and infrared images were recorded on video tape and analyzed using a video processing system. The equipment was mounted in a Cessna 411, and was used routinely to measure the progress of the spread of the slick. These measurements were compared with ground observations, and were used to measure the effectiveness of the dispersant.

INTRODUCTION

The design of the freshwater dispersant experiment has been described in another paper in this conference (Quaife et al, 1986). This paper will discuss the use of a combination of ultraviolet and infrared sensors to monitor the motion of the oil, and to study the effectiveness of the dispersant application. The remote sensing system was used as an aid to strategic response, as well as to collect data on the spreading and motion of the slick. The basic remote sensing system (Goodman et al, 1985) was mounted in a Cessna 411. In addition to the remote sensing system, a prototype

real-time image analysis system, developed by Compuheat, was available for the computation of image areas. A block diagram of the sensing system and image analyser is shown in Figure 1.

DATA COLLECTION

The registration of the two cameras of the system was undertaken using fixed ground targets. This registration was checked and found to be stable during the total experiment. The gain and zero suppression levels were set during the initial flight over the spill and these settings were used for the remainder of the experiments. The polarizing filter on the ultraviolet camera was adjusted for optimum contrast on the sheen, and changed during each pass as the sun angle changed. The polarizing filter was not very effective in increasing contrast.

The single channel image analysis system was connected to the ultraviolet channel during the dumping of the oil, since the infrared camera was not available. Missions were flown over both the oil-control slough and the slough which had oil and dispersant applied. The remote sensing flights were initiated before the spill and continued for about two hours after the spill. Another remote sensing mission was undertaken three days after the spill, at which time the infrared camera was available together with the ultraviolet camera.

During the oil release, the aircraft made continuous passes over the slough, and recorded the data at a minimum of ten minutes intervals. The data collection system did not include a time marker, and this has been a problem in subsequent image analysis. Since no sight tube was available for the aircraft, it was difficult to accurately align the flight path with the center of the spill. The small size of the sloughs was an advantage, since the shoreline could be used for positioning the slick, and the determination of the scale factor of the image.

OBSERVATIONS

Two sloughs were not identical, and the oil-alone slough was covered by to a much greater extent by areas of floating vegetation than the slough on which the dispersant was used. On both sloughs, the oil spread rapidly around the spill plate, and reached an equilibrium thickness in about ten minutes. During the application of the oil to the South (oil alone) Slough, there was a south to southwest wind which moved the slick rapidly across the surface, oiling the floating vegetation as it passed. This can be clearly seen in Figure 2. This image has been reconstructed from a single video frame taken in the ultraviolet. Infrared data taken two days later shows an accumulation of thick oil on the edges of the floating vegetation, and covering much of the shoreline (Figure 3).

On the West (oil and dispersant) Slough, the oil was advected to the each by the prevailing wind, and sheen covered most of the slough (Figure 4). However there were only a few patches of thick oil seen in the infrared image taken three days later. This lack of thick oil patches was confirmed by ground observations.

The remote sensing data has not been analysed in detail, since the necessary processing algorithms was still being developed. The main problem is the definition of a reliable method of separation of the oiled and not oiled areas in the images. In the situation where only oil and water exist this is a simple problem, but there are numerous shoreline features that return signal amplitudes of the same magnitude as the oil and water reflectors. This is true in both the infrared and ultraviolet. The areas computed from the on-board real-time analysis system include many false signals and did not give a reliable value of oiled areas.

While the presence of the oil was clear to an experienced observer, the selection of a set of pixel intensities to represent oil is not unique even across a single image. Sun glitter can cause a factor of three variation in pixel intensity from one side of an image to the other. Land features return signals of the same strength as the oil, and it is therefore necessary to undertake both a pattern recognition and intensity analysis to uniquely

determine the presence of oil. This problem was quite severe in the freshwater experiments due to the presence on area of land in all of the images.

CONCLUSIONS

An examination of the infrared video imagery clearly shows that the application of a dispersant reduced the volume and area of the thick oil associated with the floating vegetation and the shoreline. The oil was readily identified in the ultraviolet images and provided a high contrast image. Due to the interfering effects from land objects and sun glitter, difficulties have been experienced in automatically processing the images.

It is clear from both visual observations and the infrared images that the dispersant worked well, but it remains to quantify this data.

Acknowledgments

The authors would like to acknowledge the support of Esso Resources Canada Limited during this program. Jack Morrison of ERCL was responsible for the electronics system which performed without problems during the trial. The aircraft pilots of Interra Technologies played a critical role in obtaining the high quality images produced during this program. The authors wish to thank Esso Resources Canada Limited for support of this program.

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REMOTE SENSING SYSTEM

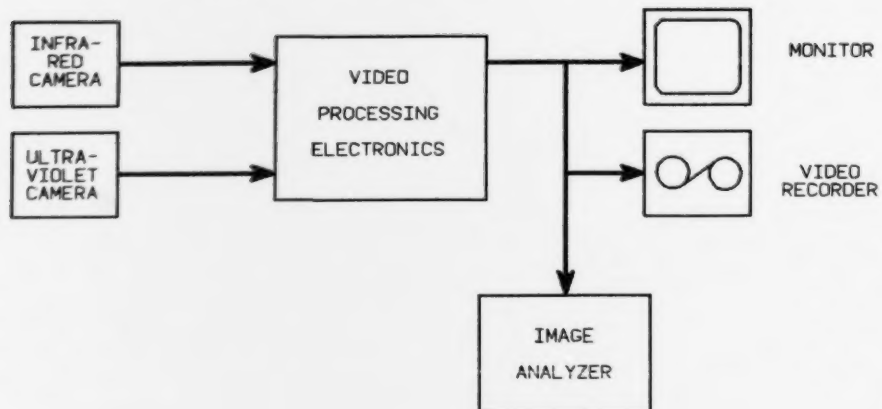


FIGURE 1. BLOCK DIAGRAM OF REMOTE SENSING SYSTEM.

F119,448,01,860521,894 MLM

Note: Photo unavailable at time of printing. Contact author for copy of picture.

FIGURE 2. Ultraviolet image taken at the spill time of the oil-alone slough

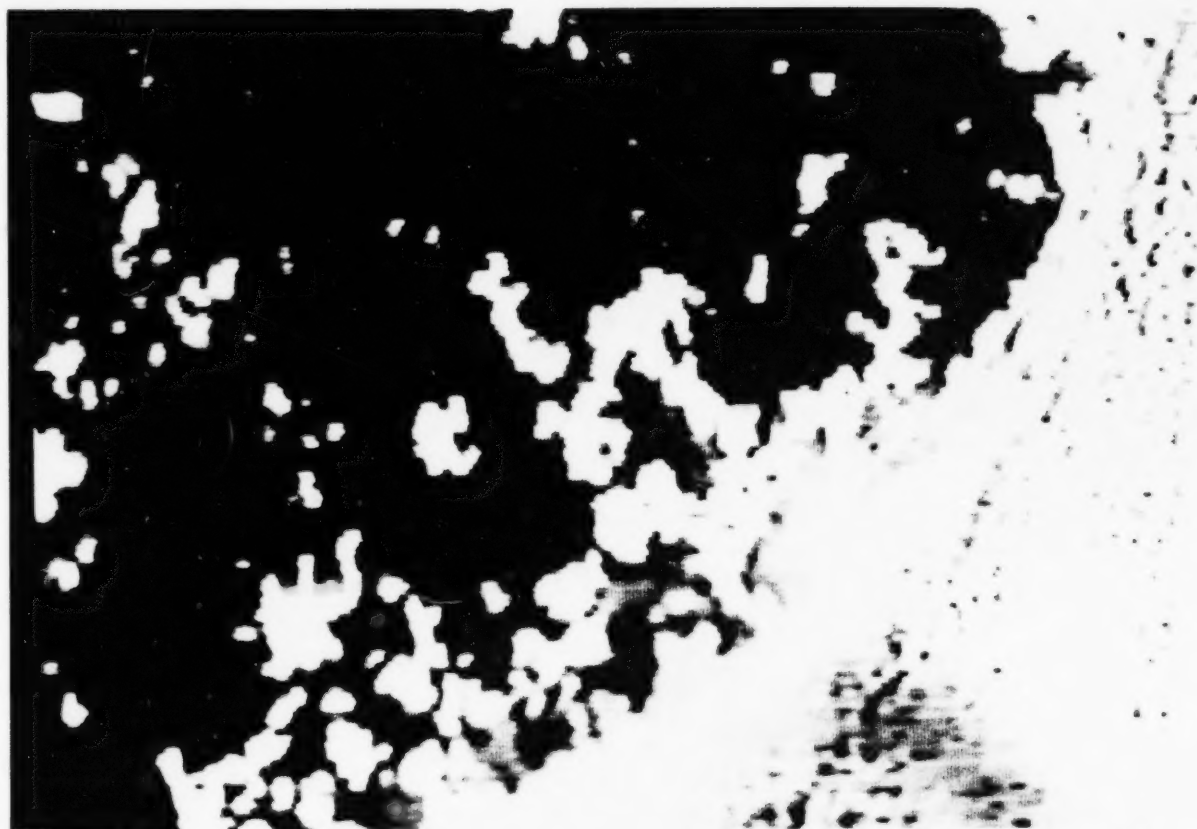


FIGURE 3. Infrared image of oil-alone slough taken two hours after spill.
The white rings are thick oil attached to the floating vegetation

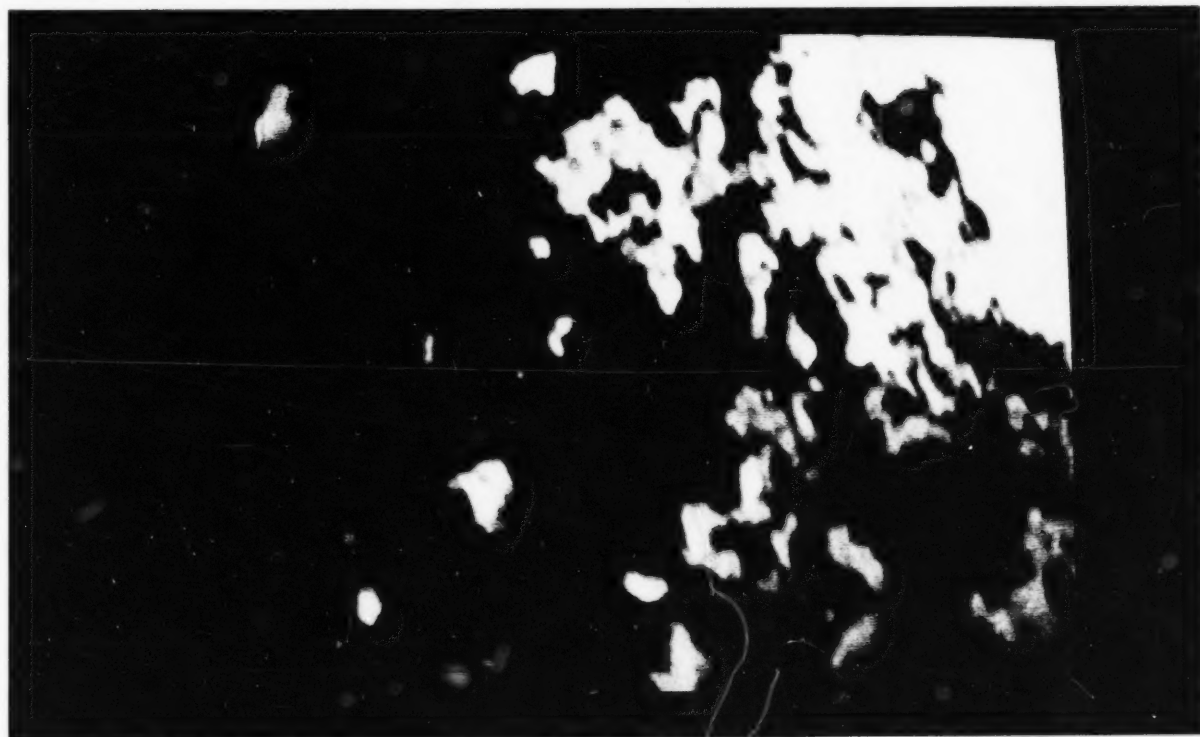


FIGURE 4. Infrared image of oil and dispersant slough two hours after spill.
Note lack of bright lines on shore as seen in Figure 3.

The Biological Component of the Freshwater Oilspill Research Program

by

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Introduction

While the probability of crude oil spills onto terrestrial and aquatic communities is low in the exploration and development of northern land-based energy reserves, their consequences must be considered. Physical control and recovery of spilled oil are essential to mitigate the ecological and aesthetic impact. However, physical control and recovery of oil spilled in and around isolated aquatic systems might be impractical and can create a greater ecological disturbance than that caused by the oil. When conventional control measures are inadequate or not feasible because of environmental conditions or geographic location, treatment with chemical dispersants may provide the only effective alternative (1,2).

Dispersants have proven to be an effective method of treating spilled oil in marine systems (3), but little is known about the fate and effects of dispersants and dispersed oil in freshwater ecosystems. A major concern in establishing dispersants as a viable oil spill technique in freshwater is the potential for shoreline damage.

The Freshwater Oilspill Research Program was designed to monitor the effects of a freshwater oilspill treated with a dispersant, Corexit 9550. Three freshwater sloughs were used for the experiment. The "West" slough was treated with 3m³ of Norman Wells crude oil and the dispersant, the "South" with 3m³ of oil, and the third, the "East" slough, remained untouched, and served as a control.

Botany Program

Dispersants, under laboratory conditions, are strong contact herbicides for several representative plant species of freshwater shoreline communities (4,5,6). Under field conditions, the dispersant could be blown or inadvertently sprayed onto the vegetation during cleanup operations. In this respect, the potential for damage is great, and likely represents one of the worst possible situation to arise from dispersant use in and around a freshwater environment.

The botanical component of the program examined the effects of oil, dispersed oil and dispersant on the aquatic and shoreline vegetation. The study effort was directed primarily at documenting changes in the plant

*Now with the Dept of Plant Science

communities, and in the degree of plant mortality attributed to oil, of oil-plus-dispersant treatments. Crude oil damage to estuarine and Arctic terrestrial communities is well documented (7-13), but virtually nothing is known about the effects of crude oil and dispersed oil on shoreline vegetation in freshwater systems. The effects of dispersant on the shoreline vegetation was investigated by directly spraying a section of the shoreline vegetation with the dispersant at the manufacturers recommended field application rate.

Untreated oil caused more damage to the vegetation, but the affected areas quickly recovered. The oil and the dispersant had no visible effect on the vegetation. Although the short term effects of the crude oil, dispersed oil and dispersant were minimal, contamination of the pore waters in and around the shoreline may pose a delayed threat to the vegetation. Long term monitoring is continuing to determine these effects.

Microbiology Program

The microbiological program was designed to monitor microbial communities in the sloughs treated with oil, and oil-plus-dispersant. Several parameters were studied including the enumeration of microbial populations, the analyses of microbial activities (enzymes), and microbial oil degradation.

As a result of these experiments, it appears that oiling the West and South sloughs had very little effect on the indigenous bacterial populations or their activities. Little change in population numbers was observed, and most activity changes could be explained in terms of seasonal influences. There appeared to be some enrichment for aromatic hydrocarbon degraders in the oiled sloughs. No major beneficial or deleterious effect of the addition of oil or dispersant were observed in the tests conducted.

Experimental Site

The shoreline plant communities were composed of species common to bog lakes. Cattails (Typha spp.) growing on floating mats of sedge (Carex spp.) were dominant in areas adjacent to open water. In drier regions, the sedge was replaced by Salix, Ledum, and species of moss, other grasses, herbs, and scattered colonies of fruticose lichens. Further back from shore, this zone ended in a bog forest of black spruce and larch or mixed stands of birch, poplar, black spruce, and larch. The section of shoreline sprayed with the dispersant was selected to include the greatest diversity of representative plant species. On return visits to the experimental area, any visible signs of oil or dispersant damage to individual plants were recorded (photographed) and the plants tagged for future reference.

Experimental Program

Two isolated bog lakes approximately 100km north of Edmonton, Alberta, were each treated with 3m³ of Norman Wells crude oil. Thirty minutes after oiling, the slick in one slough was treated with the chemical dispersant Corexit 9550. The dispersant was applied by a helicopter equipped with an extendable spray boom (D10 nozzles and size 45 cores) flying 15 m above the water at 40 km/h to give the desired application rate of the 1:10 dispersant to oil ratio. A 600 m² section of shoreline vegetation was sprayed in

identical fashion.

Observations Botany:

No extensive damage to the vegetation was observed in the lake treated with oil and the dispersant. Some drops of dispersant were noted on the foliage of Typha growing along the shoreline, but similar spotting was not observed on the sedge. These spots later turned necrotic, but the extent of damage was not lethal to the plants. Other plant species with broad leaves were carefully examined around the shoreline and within the section directly sprayed with Corexit 9550. Some traces of the dispersant were observed on the foliage but the extent of damage was considerably less than that incurred through natural causes. Small patches of floating oil around portions of the shoreline were noted one week after treatment but not after one month.

Oil damage to shoreline vegetation in the lake treated with oil only was minimal. This bog lake contained numerous floating islands composed of Typha and Calla. The oil killed the vegetation in one island next to the spill site along with the exposed leaves and stems of water lilies (Nuphar spp.). Oil washed ashore coated the lower portions of the vegetation and caused some mortality. However, only plants adjacent to open water were affected. New growth was observed one month after oiling. Islands and remaining shoreline not exposed to oil by the prevailing winds appeared undamaged. A definite surface slick persisted after 3 months. Wave action washing oil from intact portions of dying vegetation may have contributed to the slick.

Although the short term effects of the crude oil, and dispersant on the shoreline plant communities were minimal, contamination of the pore waters in and around the shoreline may pose a delayed threat to the vegetation. Over time, damage to the root systems may influence regrowth of individual species. The long term and often delayed effects of crude oils on the growth and survival of Arctic plant communities are well documented (6, 10, 13). In many of these studies, however, the vegetation in low lying wetlands were the most resilient and had the greatest recovery potential. The elevated water table in near shore areas may limit the depth of penetration of the oil and protect the root systems. Changes in the water table are of less importance in bog lakes because the shoreline vegetation usually grows in floating mats. The plant communities adjacent to open water are often comprised of only a few species such as sedges (Carex spp.). The ability of these species to grow from rhizomes or healthy portions of aerial tissues will allow for the rapid recovery of these shoreline communities following oil damage.

Many factors must be considered in the decision to chemically treat spilled oil including the adequacy of conventional control measures, dispersibility of the oil, environmental conditions, location, and response time (2, 14, 15). Frequently, the clean-up operation creates a greater ecological disturbance than that caused by the oil. The best response to oil spilled in and around freshwater systems difficult to access is probably, no action at all. Although the untreated oil caused more damage to the shoreline vegetation in the isolated bog lakes we examined, recovery of the impacted area was rapid. Oil in open waters or on shoreline areas may, however, adversely affect indigenous wildlife. In this respect, chemical dispersion of spilled oil may provide the most effective control measure.

Observations Microbiology:

Several microbial populations in the sloughs were monitored over the sampling season. The aerobic populations in water column and sediment were enumerated by spread plate onto Plate Count Agar, while the anaerobic populations from the sediments were counted on Brain Heart Infusion plates incubated in anaerobic jars. Sulfate reducing bacterial populations were estimated using the Most Probable Number technique. Lipolytic bacteria from the water column were grown on Spirit Blue/Cottonseed agar. All plates were inoculated in replicates of three or five, and incubated at 15°C.

The aerobic microbes from East and West Slough water column samples showed no discernible trends in population size during the sampling season, while the South Slough water column showed an aerobic population which increased slightly as the season progressed. In contrast, the aerobic populations from sediment samples showed decreasing population sizes with season in all three sloughs. There was also a slight decrease in anaerobic sediment populations during the sampling season in all three sloughs. The sulfate reducing bacteria (SRB's) decreased in abundance in the South and East slough sediments between June and September, but the West Slough SRB population showed a slight increase immediately post-spill. The lipolytic bacteria apparently increased in numbers in the South and West Sloughs from pre-spill to post-spill, but the population numbers in the East Slough fluctuated considerably.

Generally, these shifts in population sizes are probably not significant nor related to the oil and dispersant use, especially since they are usually paralleled by results from the unoiled East Slough. One might suppose that the spilled oil would have provided an additional carbon source for natural microflora, thus allowing increased population sizes, but this does not seem to have occurred in the populations which we monitored.

Specific microbial activities were monitored throughout the sampling season. In particular, the production of methane from slough sediments was measured. All test samples were supplemented with acetate and molybdate while duplicate controls received only molybdate, to demonstrate methane production from endogenous substrates. Methane was produced in all slough samples, and addition of acetate stimulated the production of methane in all samples, provided that incubation was extended a sufficient amount of time. The "lag time" (i.e. time before the level of methane produced in test samples was noted to exceed the levels in control samples) was monitored. This lag time was found to be slough-specific: the West Slough had the shortest lag times and the South Slough had the longest lag times, regardless of season. This might imply that the West Slough had the lowest amount of natural substrate for methanogens, and therefore exhausted its acetate-unsupplemented methanogenic capability first. Generally, the lag times shortened with the advancing season. There was no apparent effect of oiling on methane production, either in lag time or extent of methane production.

Alkaline phosphatase activity was monitored in water samples at 15°C. Phosphatase activity generally increased with season, but there was no

aerobic and anaerobic nitrogen fixation, and no conclusions were drawn from these studies.

Microbial oil degradation was studied in three manners: (1) in situ studies were carried out by incubating slough water in closed containers in the West and South sloughs with addition of oil and nutrients (nitrogen and phosphorus); N,P plus dispersant in West Slough samples; (2) laboratory studies were carried out on water column samples brought back to the laboratory for incubation at 15°C with oil and N,P under controlled conditions; (3) radiometric studies were performed in the laboratory using ^{14}C spiked oil. In the first two studies, oil degradation was monitored chromatographically. In the ^{14}C studies, mineralization of the specific, labelled compounds was measured by collecting $^{14}\text{CO}_2$.

The in situ degradation experiments were designed to show that degradation of oil by natural microflora could take place under prevailing environmental conditions in the sloughs. Oil degradation did take place under the in situ conditions in both West and South Sloughs. However, the south slough had an oil-degrading capability that was superior to the West slough, both immediately post-spill (July 12 samples) and 3 weeks post-spill (August 7 samples).

The laboratory degradation experiments were intended to show that the capability of the microflora to degrade oil increased after exposure to the spilled Norman Wells oil; that is, that population adaptation resulted from exposure to the hydrocarbons. Three specific fractions of oil were studied in the experiments: the saturates, the aromatics and the sulfur heterocycles. It was found that there were no significant differences between the three sloughs in degradation of the saturates on any particular sampling date. That is, all sloughs, whether oiled or not, possessed microbes capable of saturate degradation at all sampling times. The addition of N,P was necessary to observe this degradative potential; without N,P additions, saturate degradation was very slow. In contrast, N,P addition was not always necessary for the samples to begin degrading the aromatic fraction. The unoiled East Slough had an inferior capability for degrading aromatics, compared with the oiled West and South Sloughs. In addition, it was found that aromatic degradation did not occur in samples taken prior to the oil spill. This may in part be a seasonal effect, since very limited aromatic degradation occurred in East Slough samples starting in mid-July (but not before this time), and aromatic degradation peaked in the West and South sloughs between July 25 and August 14. Similar results were obtained for the sulfur heterocycle fraction: N,P supplementation was not always necessary to initiate degradation; there was no significant degradative capability pre-spill; and West and South slough populations were superior to East Slough populations in sulfur heterocycle degradation.

Radiometric studies confirmed the laboratory oil degradation studies. It was found that water samples supplemented with N,P were equally capable of mineralizing ^{14}C -hexadecane (a model saturate compound), regardless of season or slough site. However, ^{14}C -phenanthrene (a model aromatic compound) was not mineralized in any slough until the July 25 samples were tested, which indicates that the failure of slough populations to degrade aromatics (as demonstrated in the laboratory studies) is probably a seasonal effect rather than a post-spill population enrichment effect.

than a post-spill population enrichment effect.

The field fertilizer experiment is incomplete and will not be discussed.

Summary and Conclusions

To summarize, it appears that oiling of the West and South sloughs had very little effect on the indigenous bacterial populations or their activities. Little change in population numbers was observed, and most activity changes could be explained in terms of seasonal influences. There appeared to be some enrichment for aromatic hydrocarbon degraders in the oiled sloughs. No major beneficial or deleterious effects of the additions of oil or dispersant were observed in the tests employed.

Similarly, little or no effects were noticed on the aquatic and shoreline vegetation. While some immediate oiling of the surface and shoreline vegetation was apparent, the affected areas recovered quickly. Contamination of the pore waters and possibly the root systems in and around the shoreline may pose a delayed threat to the vegetation. Long term monitoring will provide more information.

The biological component of the Freshwater Oilspill Research Program has shown that dispersants can be used in certain situations in freshwater environments, with little or no adverse effects. The results of the long term effects of the oil, dispersed oil and dispersant will provide more information, and will help to determine the freshwater oil spill situations where dispersants can be used as the mitigating technique.

Acknowledgments

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**EXPERIMENTAL AND THEORETICAL BASIN
STUDIES OF DISPERSANT EFFECTIVENESS
IN COLD WATER**

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ABSTRACT

During November, 1984 and April, 1985, tests of dispersant effectiveness were carried out at Esso's wave basin facility in Calgary, Alberta, Canada. Regular, non-breaking waves were used, and oil concentrations in the water column were continuously monitored by the fluorescence emission technique.

Analysis procedures designed to examine the measured oil concentrations were established. Cross correlation lag time calculations were used to identify the time it took oil to migrate from one measurement port to another in the water column under the effect of waves and dispersants. A kinematic model which solves the diffusion - advection equation numerically was used to calculate the efflux of oil from the containment boom.

The calculations enabled a comparison to be made between the effectiveness of Corexit 9527 and CRX-8. It was found that in the modelled examples, oil travelled down the water column faster and more dispersed oil stayed in the water column when CRX-8 was used.

INTRODUCTION

During November 1984, a series of tests was carried out in the Esso wave basin to determine the effectiveness of two dispersant chemicals, Corexit 9527 and CRX-8. The results of these experiments have been reported in detail in "Dispersant Effectiveness in Cold Water", by Brown et al (1985).

The November trials were conducted to determine the effectiveness in cold water of dispersants for use in oil spill response in both the Beaufort Sea and the Flemish Pass area of the North Atlantic. Information on the behavior of dispersants in cold water environments is sparse, although some laboratory studies have been done. Only one open sea oil spill test at temperatures below 8C. had been attempted. Therefore, the November tests was to study, under more controlled conditions, some of the basic mechanisms which affect dispersant action. The wave basin (Brown et al 1985) is a particularly suitable facility for this purpose as the testing can be done on a realistic scale but without the logistical difficulties encountered in an open ocean spill.

As a result of the November tests, a number of questions was raised which became the incentives for a second series of dispersant tests conducted during April 1985. Chief among these was the calculation of dispersant efficiency. It had proved very difficult to adequately track oil movement through the water

column with the existing array of fluorometer sampling stations and hence to make an accurate material balance of the oil. Likewise, no accurate measurement of any oil remaining undispersed in the containment boom at the end of each test was made. The test procedures and equipment, as well as the methods to be employed in data analysis were designed to address these shortcomings.

1.1 TEST FACILITY AND EQUIPMENT

Brown et al (1985) describes the wave basin and the equipment used in the November trials in detail. In what follows, only those changes to equipment made for the April trials will be described.

Containment Boom

The 10 m diameter skirted boom used during the November tests to contain the spilled oil was replaced with an unskirted model. It was felt that this would allow the oil to disperse radially through the water in a manner closely approximating a real spill.

Oil Application and Cleanup

Fresh Norman Wells crude (75 liters) was applied to the water surface via a hose and metering pump from barrels at the basin edge. Any oil remaining within the boom after the experiment had ended was recovered with a Morris Industries Model MI-2C disk skimmer. The skimmed oil was pumped into a large carbuoy, allowed to stand for 24 hours and then decanted. Water content of the oil and oil content of the water was determined as well as the volume of the oil recovered.

Oil Drop Size Analysis

A Hiac/Royco Model 4100 particle counter with both a Model CMH150 sensor and a Model 346-B laser sensor was used to measure the particle size distribution. Detection and counting of oil droplets as small as 0.5 microns in diameter were possible using the equipment.

Fluorometry

Five fluorometers were used to monitor the dispersed oil; three of these were connected permanently to sampling ports within the containment boom area as in the November trials. The fourth fluorometer was connected permanently to a sampling port in the middle of the basin outside of the containment boom. The fifth fluorometer was connected to a series of electrically actuated valves which automatically directed water to it from 4 locations outside of the boom area. Each of the 4 locations was sampled for 30 seconds every two minutes. With this sampling arrangement greatly improved tracking of the dispersed oil cloud was possible.

Test Procedures

The test procedures were similar to those followed in the November 1984 dispersant trials. A total of 12 experiments were carried out in which Corexit

9527, Corexit 9550 and CRX-8 were used to treat weathered and fresh Norman Wells crude oil. A dispersant to oil treatment rate of 1:20 was used and the dispersant was applied with either the dispersant application boom described previously or with a hand sprayer. (Brown et al, 1985)

2.1 FLUOROMETER MEASUREMENT

An example of the oil concentrations measured during the tests is shown on figure 2.1. Oil concentration is shown as a function of time after the dispersant had been applied to the spilled oil. Four sampling locations are indicated (from top):

- 50 cms. below the still water surface at the boom centre.
- 100 cms. below the surface at the boom centre.
- 150 cms. below the surface at the boom centre
- 50 cms. below the surface near the basin center (outside of the containment boom).

Note that the top 2 curves have been offset (from top) by 10ppm, and 5 ppm respectively for clarity in reading. The data has been corrected for hydrocarbon background.

The oil concentrations measured within the containment boom area during April show similar characteristics to those recorded in November. There is an initial rapid increase in oil concentration followed within an hour or so by a leveling off as long as wave action continues. Even with no skirt to help contain the dispersed oil within the boom area, it is apparent that oil is rapidly circulated at least 150 cm into the water column. Absolute concentrations are somewhat lower than in November.

2.2 DATA ANALYSIS

In order to interpret the fluorometry measurements from the April tests both this data and the previous data from November were examined. This analysis was designed to:

- Identify the oil dispersion rate into the water column;
- Calculate the amount of oil efflux from the containment boom area;
- Compare the effectiveness of different chemical dispersants.

2.3 IDENTIFY OIL DROPLET DISPERSION RATE INTO THE WATER COLUMN : THE CROSS CORRELATION ANALYSIS

The solution procedure to obtain the rate of oil dispersion into the water column was motivated by physical observations of measured data. In examining the measured concentrations at locations x(50 cm), y(100 cm) and z(150 cm) in the water column during the tests, some concentration peaks seemed to occur first at depth x, followed by similar peaks at y and z, a short time later. (Figure 2.2) To obtain the lag time existing between the curves, a cross correlation analysis was performed.

The analysis procedure is simple. A vector of measured data (eg from the top sensor, or x position) is used as a reference. The middle (or y) sensor data is then slid forward in time, in uniform lag-time steps, and a cross correlation coefficient between vectors at x and y is computed for each time delay. This procedure is similar to Kircher and Shah, 1975. When the peaks and troughs of the vectors at x and y coincide at a certain lag time, the cross correlation coefficient will peak. This lag time will then be assumed to be the time required for oil to migrate from one measurement port to the other. The measured oil particle size distribution shows that the oil droplets generated are small enough (Brown et al 1985) that resurfacing of the droplets during the tests will not be important. The migration of oil from one measurement port to the other is assumed to occur in a downward direction only.

This lag time calculation is a comparison of peaks and troughs between data vectors. If the peaks and troughs are not prominent, or if they occur at random, the cross correlation coefficient will not peak except at lag time zero. This effect was observed in the analysis of November test number 2 (Figure 2.3) in which the maximum measured concentration was only approximately 5 ppm.

The observed time lag between the concentration peaks of data vectors at the different locations is a result of oil droplets propagating downwards from oil sources on the surface or in the water column. If there is more than one oil source emitting plumes of oil droplets, multiple peaks of the cross correlation coefficient at different lag times will occur. The different lag times indicate the differences in oil plumes' arrival times at the measurement port locations from various sources. The multiple cross correlation peaks are expected to be more pronounced for the November than the April data, since the 150 cm long boom skirt used in the November tests will restrict the radial dispersion of oil, forcing the oil plumes to migrate downwards only. The result of this is an effect similar to having reverberations in recording sound waves. Due to this effect, it will be harder to identify the lag times of a source directly overhead of the measurement ports from the November data (Figure 2.4). However, for the April tests this effect is less prominent because of the unskirted boom, and the lag time peaks due to a dominant source is much easier to detect (Figure 2.5).

Figure 2.5 shows the measurement ports at the 50 to 100 cm levels. The analysis shows that the dominant peak for the 100 to 150 cm levels is at the same lag time as the 50 to 100 cm levels. This means that the plumes travelled the distances at the same velocity. We do not have data to calculate the lag time for the 0 to 50 cm levels. However, based on the lag times for the 50 to 150 cm levels, a constant plume velocity is assumed for the top 150 cm.

An important implication of the constant plume velocity is that the positions of the sources may be inferred from the lag times. An illustrative example is November test 4. Figure 2.6 shows the twin lag time peaks for the test at lag times of 16 and 128 seconds (50 to 100 cm level). In Figure 2.7, which shows the lag time peaks for the 100 to 150 cm levels, the small peak at 128 seconds is there but the dominant peak is at 32 seconds. The peaks at 128 seconds in Figures 2.6 and 2.7 indicate a constant plume travel time of 128 seconds per 50 cm. Therefore the peak at 32 seconds must be due to a plume from a different source.

A conceptual model of a migrating plume is shown in Figure 2.8 (Bendat and Piersol, 1980). The angle of incidence of the plume can be obtained from the formula;

$$\cos(A) = C \cdot T / D \quad 2.3-1$$

Where

A= angle of incidence

C= velocity of plume

T= lag time

D= distance between sensors

From the angle of incidence, the location of the source (assumed to be on the water surface) is found to be 4.8 m from the center line. On examining a photograph taken during this test the oil slick was actually located next to the boom which has a radius of 5 m. With the source location the plume travel time difference for the ports at 50 and 100 cm levels is computed. The time difference is approximately 16 seconds. The peak at 16 seconds in Figure 2.6 for the top two sensors indicates the presence of the source next to the boom

November tests 3,4 and April tests 2,5,8,9 were analysed and the results tabulated in table 1. The tabulated values show that the use of hand sprays significantly increased the dispersion plume velocity for both Corexit 9527 and CRX-8. Better mixing and controlled application of dispersants seemed to have been achieved by the hand sprays. The average oil droplet migration time for CRX-8 is approximately 15% lower than that of Corexit 9527. Therefore, the oil droplets generated when CRX-8 was used are smaller than those of Corexit 9527.

2.4 Calculation Of The Amount Of Oil Efflux From The Containment Boom

A kinematic simulation model was developed to calculate the amount of oil efflux from the containment boom. The diffusion data from two tests in November (3, 4) was used to calculate the efflux volumes of oil. The April data is not used because the unskirted boom allowed significant radial diffusion away from the measurement port locations.

A stable, alternating direction implicit finite difference scheme (Carnahan et al, 1969) was used to solve the two dimensional diffusion-advection equation:

$$\frac{dc}{dt} = \frac{d}{dx} \left[D(x) \frac{dc}{dx} \right] + w \frac{dc}{dx} + \frac{d}{dy} \left[D(y) \frac{dc}{dy} \right] \quad 2.4-1$$

Where:

c = oil concentration
t = time
w = terminal velocity

x = depth dimension
 y = horizontal dimension
 D(x) = vertical eddy diffusion coefficient
 D(y) = horizontal eddy diffusion coefficient

The first and last term on the right hand side of the equation represent downward and horizontal diffusion while the middle term deals with advection. Since the recorded data is one dimensional, $D(y) = 0$, reducing equation 2.4-1 to:

$$\frac{dc}{dt} = \frac{d}{dx} [D(x) \frac{dc}{dx}] + w \frac{dc}{dx} \quad 2.4-2$$

This form of the diffusion-advection equation is identical to the one in Johansen (1983). As in that paper, the equation is non-dimensionalized, and can be used to simulate diffusion-advection of oil droplet in the water column. The kinematic model does not consider the interaction of the oil, dispersant and wave action directly. Since it is the kinematic motion of the oil droplets that is being modelled, the diffusion coefficient, $D(x)$, accounts for the vertical dispersion of oil droplets generated in a low energy wave environment.

The diffusion coefficient, $D(x)$, was computed by applying the one dimensional turbulent diffusion equation (Ippen, 1966) to the measured concentrations at the 50 and 100 cm levels. The calculated coefficient of $14 \text{ cm}^2/\text{sec}$ is used in the model, and is kept constant for the containment boom depth of 150 cm.

The constant diffusion coefficient models a plume of oil droplets travelling steadily with respect to changes in the concentration gradient. Terminal velocities relating to oil droplet sizes are obtained from Johansen (1983).

The simulation time step is determined by the lag time computed in the previous section. The use of a constant diffusion coefficient in the model and a computation time step in accordance with the observed lag time allows an interpretation of the measured data.

The numerical model considers the diffusion and advection of oil for each size of oil droplet particle. The proportion of each particle size of oil used in the model is the same as the measured particle size distribution. A typical simulation curve is shown in Figure 2.9. When the simulation results matched the normalized data curve as shown in the figure, the concentration profile outside the boom skirt is integrated to obtain the oil volume. A summation of the integrated oil volumes for the duration of the test will give the total amount of oil which dispersed from the control boom into the basin. The total dispersed volume minus the volume of oil obtained from the background oil concentration 24 hours after the test will give the amount of oil that resurfaced after being dispersed. The ratio of the volume of oil resurfaced to the total volume dispersed gives the percentage of oil resurfaced.

Two calculations for November tests 3 (Corexit 9527, 20 cm waves) and 4 (CRX-8, 20cm waves) were performed. The model results for these tests, which used a 150 cm long boom skirt, show that CRX-8 was more effective in

generating more oil which stayed in the water column (25 l) than Corexit 9527 (18 l). Although the amount of oil resurfaced after 24 hours is more for CRX-8 (37.7 l) than Corexit 9527 (26.76 l), the percentage of oil resurfaced is the same for both (60 %). The computation results are summarized in table 2A.

3.1 DISCUSSIONS AND CONCLUSIONS

The dispersant efficiencies of two of the November tests were discussed in the last section. The amount of oil resurfaced after dispersing through the skirted boom was approximately 60 % of the dispersed volume. A detailed material balance is summarized in table 2A.

Material balance and other experimental parameters for the April tests are summarized in tables 2B and 3. The dispersant efficiencies were calculated by assuming that all oil not recovered by the skimmer or lost through evaporation was dispersed. Ideally one would like to be able to calculate the amount of dispersed oil on the basis of the concentration measurements to complete the material balance, as in the case of the November test examples. Unfortunately, clouds of dispersed oil droplets may move beyond the containment boom, without detection by the fluorometers, and then resurface. Such oil would be lost in the material balance. In one instance, this situation was observed and a grab sample of the water/oil mixture taken, which had a concentration of 417 ppm. More sampling ports and better location of them may overcome this problem in future experiments.

From the data it is apparent that:

- On the average, CRX-8 disperses oil that travels down the water column 15 % faster than Corexit 9527.
- Application method of the dispersant is critical. Oil penetrates the water column faster for both Corexit 9527 and CRX-8 when applied by hand spray.
- Based on the data of the November tests, more oil is dispersed into the water column when CRX-8 was used. The percentage of oil resurfaced after being dispersed was the same for both CRX-8 and Corexit 9527.
- Corexit 9550 was clearly inferior under these test conditions (April test 6,7).
- In very low energy waves dispersion is low. April test 3 results are probably pessimistic because water circulation was so low that most resurfaced oil would remain in the boom.

More research effort is needed to study the relationship between the mass transfer of low energy, regular, waves and the dispersion of oil droplets under the effect of dispersants. A constant value of dispersion coefficient, independent of depth, has been observed under field conditions. (T. Ichiye, 1967) However, It is difficult to relate the dispersion effects of 20 cm regular waves to those of wind generated random seastates. But since the dispersion of oil through the long skirt was significant and the analysis showed a constant plume velocity for the top 150 cm, an "effective" dispersion

coefficient may be developed for each regular wave height.

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APRIL TRIAL 9 - 9527 - 20 cm WAVES

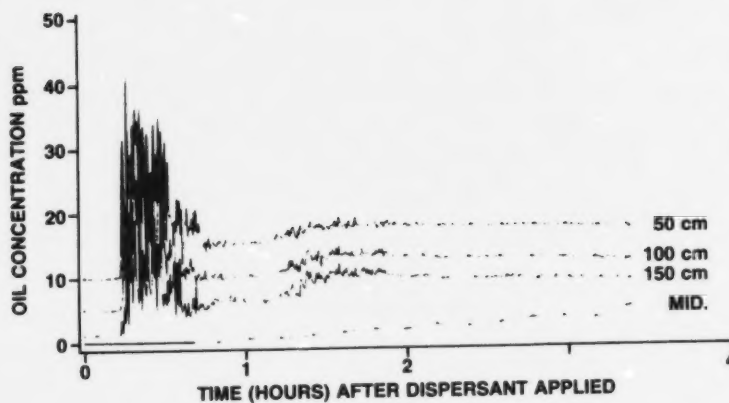


FIGURE 2.1

NOVEMBER TRIAL 3 - 9527 - 20 cm WAVES

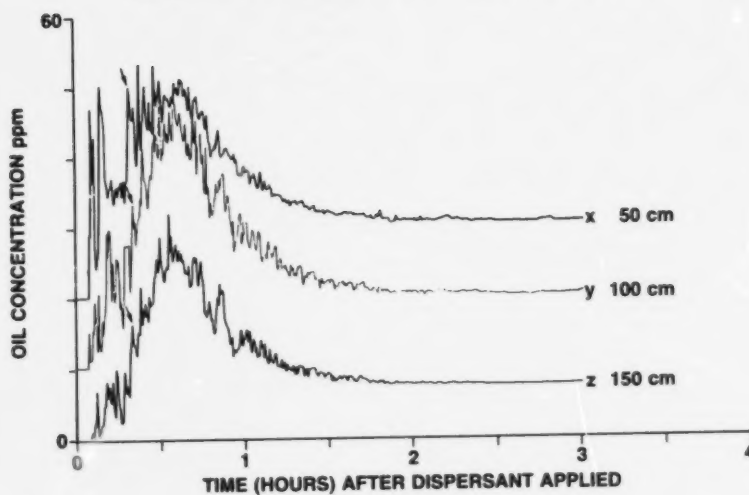


FIGURE 2.2

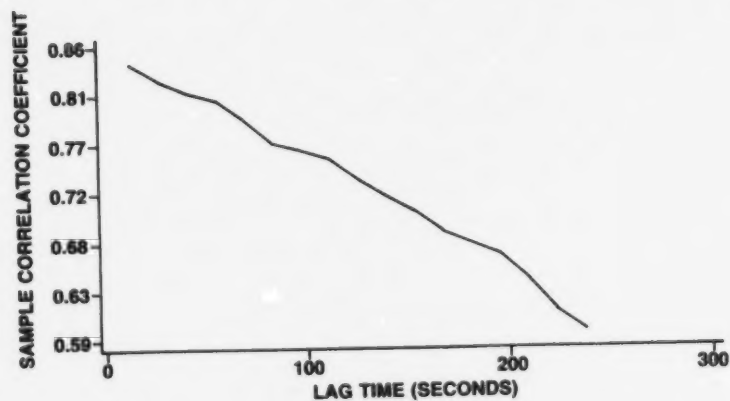
CROSS CORRELATION COEFFICIENT vs LAG TIME
NOVEMBER TRIAL 2 - 9527 - 20 cm WAVES
WEATHERED OIL

FIGURE 2.3

CROSS CORRELATION COEFFICIENT vs LAG TIME
NOVEMBER TRIAL 7 - 9527 - 10 cm WAVES

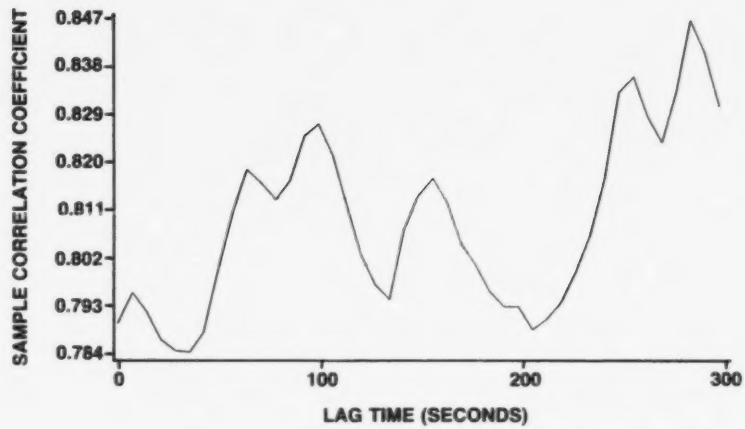


FIGURE 2.4

CROSS CORRELATION COEFFICIENT vs LAG TIME
APRIL TRIAL 2 - 9527 - 20 cm WAVES

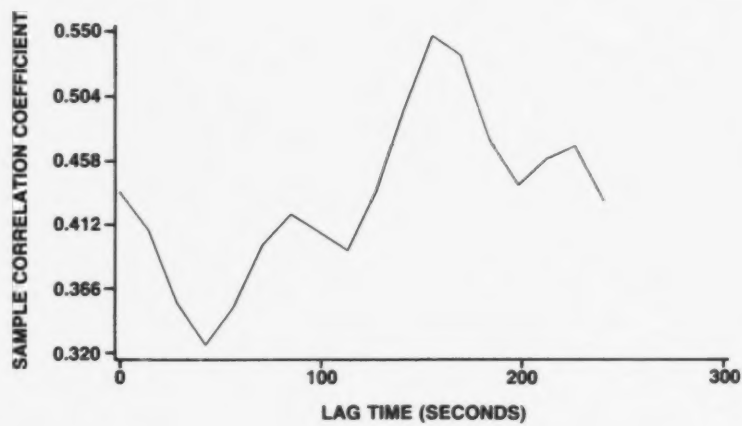


FIGURE 2.5

**CROSS CORRELATION COEFFICIENT vs LAG TIME
NOVEMBER TRIAL 4 - CRX - 8 - 20 cm WAVES**

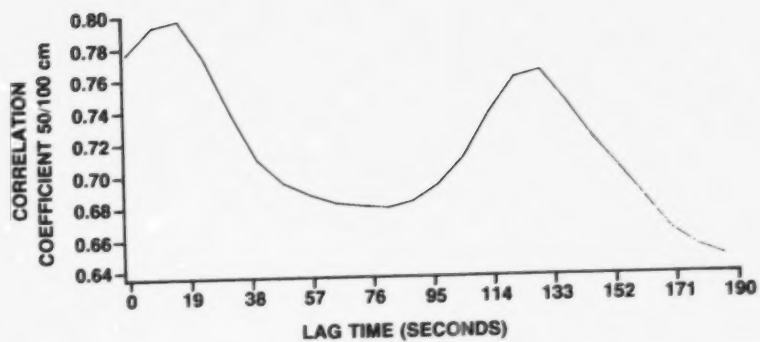


FIGURE 2.6

**CROSS CORRELATION COEFFICIENT vs LAG TIME
NOVEMBER TRIAL 4 - CRX - 8 - 20 cm WAVES**

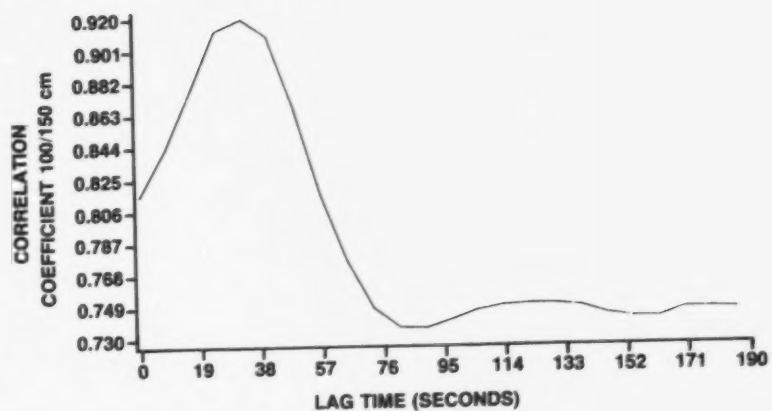


FIGURE 2.7

**SOURCE POSITION AND ANGLE OF
INCIDENCE BASED ON PHASE MEASUREMENTS
BETWEEN TWO LOCATIONS**

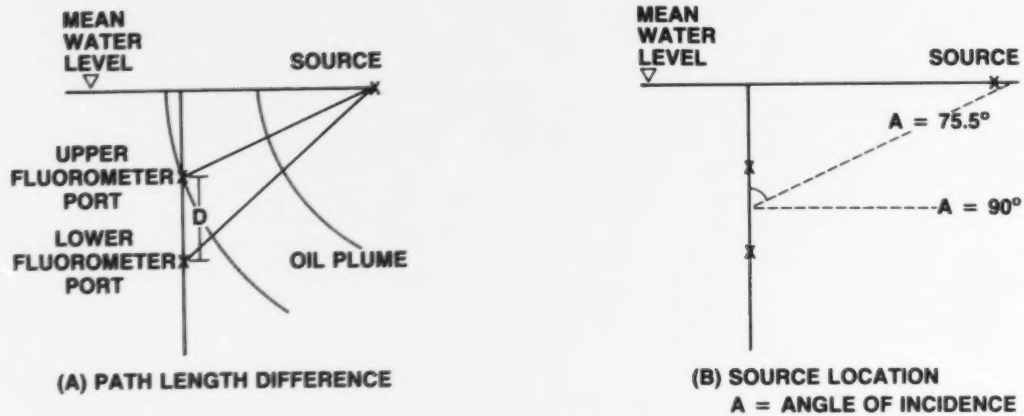
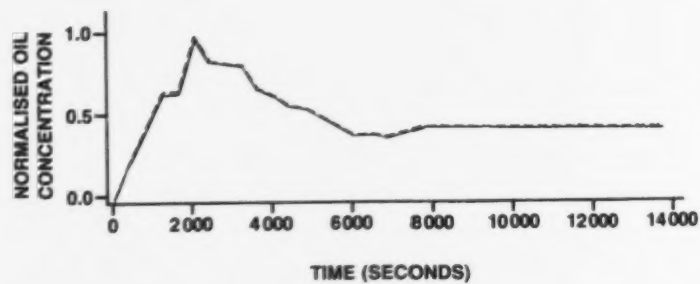


FIGURE 2.8

**NORMALISED CONCENTRATION PROFILES
NOVEMBER TRIAL 4**



SOLID LINE IS DATA NORMALISED BY PEAK CONCENTRATION
DASHED LINE IS SIMULATION

FIGURE 2.9

TABLE 1
CROSS CORRELATION LAG TIME CALCULATION RESULTS

Test No.	Boom Skirt	Dispersant	Dispersant Application Method	Oil Migration Time (in sec.) For 150 cm	Plume Migration Velocity cm/sec	Comments
Nov. 3	Yes	9527	Boom	378	.397	126 sec per 50 cm
Apr. 2	No	9527	Boom	462	.325	154 sec per 50 cm
Apr. 9	No	9527	Hand Spray	252	.595	84 sec per 50 cm
Nov. 4	Yes	CRX-8	Boom	384	.391	- 128 sec per 50 cm - multiple peaks
Apr. 5	No	CRX-8	Boom	336	.446	- 112 sec per 50 cm - multiple peaks
Apr. 8	No	CRX-8	Hand Spray	210	.714	70 sec per 50 cm

- Wave height used was 20 cm throughout

TABLE 2A
SUMMARY OF NOVEMBER 84 WAVE BASIN SIMULATION RESULTS

a	b	c	d	e	f	g	h
November Trial No.	Dispersant	Time (hrs)	Oil (P) in water	Oil evaporat- ed & oil in Containment Boom (P)	Oil Resur- faced after Dispersing (P)	Efficiency $\frac{d + f}{75} \times 100$	Comments
3	Corexit 9527	4	18.0	30.24	26.76	59.7	Simulation extended test duration from 3.5 T 4 hours
4	CRX-8	4	25.0	12.30	37.70	83.6	

TABLE 28
SUMMARY OF APRIL 1985 WAVE BASIN TRIALS

a	b	c	d	e	f	g	h
April Trial No.	Dispersant	Time (Hrs.)	Oil (P) in Water	Oil (P) Evaporated	Oil (P) Recovered	Efficiency $\frac{75-(e+f)}{75} \times 100$	Comments
1	Corexit 9527	4	6.2	25.9	27.8	28	Weathered 17 hrs.
2	9527	3	6.6	7.1	28.4	53	10cm Wave Height poor dispersant application
3	CRX-8	3.3	11.7	12.8	51.3	15	
4	CRX-8	3	17.5	10.9	43.4	28	
5	CRX-8	4	24.7	3.5	13.8	77	
6	Corexit 9550	3	2.8	8.7	34.8	42	Hand spray Disp. Hand spray Disp. Water Spray on oil Weathered 19 hrs. Fresh Water
7	9550	3	2.3	6.8	27.1	55	
8	CRX-8	3.2	6.7	3.6	14.4	76	
9	9527	3	17.8	3.4	13.7	77	
10	NONE	3	0.2	14.8	59.1	1	Weathered 19 hrs. Fresh Water
11	9527	4	7.9	23.6	27	43	
12	9550	3	3.8	11.0	43.9	27	

TABLE 3

Trial #	Disper.	Appl.	Eff.	Wind	Temperature		Comments
					Air	Water	
1	9527	B	28	N17	1	5	25% weathered oil/65% coverage/good application
2	9527	B	53	E11	3	3.5	fresh oil (30 mins.)/40% N boom/good application
3	CRX-8	B	15	C	4	4	fresh oil (20 mins.)/60% spotty/good application/10 cm
4	CRX-8	B	28	S20	12	4.5	fresh (20 mins.)/N 40% boom/poor application - 25% lost
5	CRX-8	B	77	SE11	10	4	fresh (30 mins.)/wind appeared to blow dispersant
6	9550	H	42	N28	1	3.5	2 hours weathered/25% diluted dispersant/snow
7	9550	H	55	NW30	7	2	fresh (40 mins.)/20% diluted dispersant/new water
8	CRX-8	H	76	SE35	4	1	1 hour weathered/undiluted hand spray
9	9527	H	77	S24	5	4	fresh oil (10 mins.)/undiluted hand spray
10	Water	B	1	C	10	5	fresh oil (10 mins.)/1 min. spray with salt water/S40% boom
11	9527	H	43	C	13	6	25% weathered oil/oil will spread/herding widespread
12	9550	H	27	NW30	13	12	fresh oil (10 mins.)/25% diluted on fresh water

BIODEGRADATION IN EMULSIONS OF CRUDE OIL
(TYPE KIRKUK) AND NON-IONIC DISPERSANTS.

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ABSTRACT.-

We have used a model system to follow biodegradative processes in crude oil, emulsified by means of a non-ionic polyoxiethylenated dispersant (Renex 714 or Renex 706), by microorganisms present in sea water. Variations in oxygen concentration dissolved in the sea water with time, when samples were subjected to additional aeration, were monitored. Furthermore, changes in the concentration of crude oil and dispersant were also determined, as the degrading processes proceeded. At a temperature of 20°C and an air speed of 0.5 l/min, the concentration of crude oil in stable emulsions was a lot of times most larger than in the absence of dispersant.

INTRODUCTION.-

Biodegradation of organic material takes place when it forms parts of an environment that contains microorganisms capable of using it as a source of energy and tissue-building. Biodegradation is considered as the most important natural process by which organic material polluting the environment is being eliminated through its mineralization to CO₂ and H₂O. Microorganisms are able to grow and develop during this process, within this environment. A lot of research is done in this particular field: L.Kravetz (1), K.J.Bock and H.Stach (2), Zobell (3), etc.

Many carbon compounds are very susceptible to the process of biodegradation by microorganisms. Many different species, belonging to this group, are able to degenerate carbon compounds. According to C.Beerstecher (4) there are more than a hundred. This process of biodegradation will take place when organic material is exposed to microorganisms and phenomena such as dispersion and diffusion are able to speed up this process. Some times there is a period of induction during which the microorganisms undergo mutation and so will degenerate organic compounds.

Oxygen and the nutrients (N,P,S etc.) are indispensable for this phenomenon to take place. Therefore, biodegradation is very sensitive to situations of agitation in the environment. Nutrients as well as microorganisms and oxygen are part of what we call an aqueous phase, and biodegradation depends on variables such as: adaptation to the microorganisms, temperature, concentration of oxygen and nutrients..

During this process of biodegradation, CO₂ and H₂O are formed, and energy is given out; this, in turn, is used by microorganisms together with parts of the organic material for its growth. At a later stage lack of organic material causes destruction of the microorganisms and this whole process may start again. Therefore, the initial reaction is:



A quantitative study on the reaction could be carried out studying

either the variations in concentration of the organic material through time; the amount of CO_2 produced, the amount of microorganisms or the change in the concentration of oxygen. Appropriate methods for determining these variables are described in the bibliography. For example: spectrophotometry (CTAS method, Greff (5)), IR spectroscopy (Frazee (6)), potentiometrics (7), chromatographics (8,9,10,11), oxygen demand (DBO and DCO (1,12,13)), CO_2 production (1 and 14).

Various kinetics methods have been developed to explain in quantitative terms this phenomenon of biodegradation: Michaelis-Menten (15), Monod (16), Baughman G.L. (17), N.Lee.Wolf (18), U.Fasoli (19,20). R.J.Larson (21) has formulated a model to explain in a quantitative way the development of this process of biodegradation under extreme conditions, i.e. deficiency in nutrients (N and P) which will block microorganic growth and a very small concentration of microorganisms.

We have studied the degradation of dispersants and crude-oil emulsified in non-contaminated sea water, and without any initial adaptation in period (22,23,24). In this paper we carry out an independent study on the concentration of emulsified crude-oil, the concentration of dispersants and the amount of CO_2 given out. The results derived from both methods are coherent when compared and they fit in the Larson model. The initial conditions were of the same type.

In this paper we analyse the concentration of oxygen through time. We will study the degradation of dispersants, the degradation of crude-oil and crude-oil emulsified by dispersants. We consider all the phenomena concurrent in the dissolution (respiration, growth of microorganisms, degradation, etc.). We will suggest equations for the obtained results in order to explain the same phenomenon through analysis of other properties (concentration, CO_2 , etc.). Consequently, the coefficients will represent the phenomenon mentioned before. This study has been carried out with well-stripped dissolutions by steam saturated air and non-stripped dissolutions

EXPERIMENTAL PART.-

1.- Products used: The experiments have been carried out with recent sea water taken from a non-polluted area in the Palma bay; the crude-oil is of a Kirkuk type, and the dispersants are non-ionic dispersants, oily alcohol lineal alquilpolyoxiethylenated, Renex 714 and Renex 706. The characteristics have already been described by the authors (25).

2.- Preparation of the dissolutions: The used dissolutions are of the following type:

- 2.1. Dispersant (Renex 706 or 714) in sea water.
- 2.2. Crude-oil and dispersant (Renex 706 or 714) in sea water.
- 2.3. Crude-oil in sea water.

The dissolutions of type 2.2 are prepared while mixing the dispersants and the crude-oil in relation 3 to 50 and using an instrument with three propellers for stirring (HEIDOLPH RLG 55-1 type). Speed of stirring is 4000 rpm. The indicated conditions which were determined by writers, lead to a better dispersion (25 and 26). The dissolutions of the dispersants in sea water were prepared in a such way that the concentration of the respective emulsions coincide with the corresponding one of type 2.2.

As a final result equal volumes of 4.75 l. were obtained from the different dissolutions and were put into properly closed cylindrical reactors of 5.5 l. These, inturn, were kept in a dark place at a temperature of

20°C. An air current, saturate with H_2O and having a temperature of 20°C produced the so called "gas stripping" effect in the dissolutions, which were aired permanently. The gases were collected in dissolutions of concentrations known as $Ca(OH)_2$ and this made it possible to determine the quantity of the CO_2 produced.

Other sample-taking methods by which we can determine the concentration of the dispersant are: CTAS spectrophotometry, IR spectroscopy, oxygen concentration, CO_2 released methods. For the crude-oil: IR spectroscopy, GC chromatography, CO_2 released and the concentration of oxygen. In order to determine the concentration of oxygen the flow current of air is cut-off momentarily and a Oxymeter YSI 54 is used.

Winklers bottle of 100 ml. of volume are filled up with the dissolution for the types indicate above and the concentration of oxygen in relation to different temperatures are measured.

3) Results and discussion:

The results obtained by measuring the concentration of the oxygen dissolved in dissolutions of the dispersants (the process of biodegradation takes place in there) are shown in the table (I) underneath.

The concentration of oxygen dissolved is in each unit of time a function of the different phenomena which participated in this process: respiration, growth of the microorganisms, degradation (oxidation) of the organic material, the flow of bubbling air, etc.

Time (days)	Concentration of Oxygen (ppm)				
	Renex-714	Renex-706	Renex-714 + Crude-oil	Renex-706 + Crude-oil	Crude-oil
0	8.8	8.8	8.8	8.8	8.8
5	8.8	8.8	8.75	8.7	9.1
8	8.65	8.6	8.6	8.6	9.2
14	8.4	8.05	8.4	8.4	9.1
19	7.9	7.7	8.15	8.0	9.1
22	7.35	7.1	8.0	7.8	9.2
26	6.9	6.9	7.6	7.7	9.2
33	6.5	6.5	7.3	7.2	9.3
40	6.25	6.5	6.9	6.8	9.2
47	6.1	6.0	6.3	6.7	9.1
54	5.4	5.4	5.8	5.9	9.2
61	4.9	5.0	5.3	5.4	9.2
68	4.8	4.1	4.75	5.1	9.2
76	3.8	4.2	4.25	4.7	9.2
82	4.1	4.1	4.3	4.0	9.2
93	3.9	4.05	3.9	3.6	9.1
110	3.8	4.1	3.7	3.1	9.2
124	4.05	4.3	3.6	3.0	9.2
139	4.2	4.45	4.1	3.2	9.2
154	4.2	5.1	4.4	3.6	9.1
167	4.9	5.1	4.5	4.25	9.1
183	4.5	4.95	5.4	5.1	9.2
201	7.4	7.5	6.05	6.2	9.3
221	7.35	7.95	6.6	6.95	9.2

Table I: Results experimentals of the concentration of oxygen.

The aim, however, is to find an equation which could be used to cover all the phenomena mentioned above and which, in turn will include more parameters of the type occurring in equations of the velocity of dispersants of crude degradation, determined by analysis of other properties.

3.1.- Dissolutions of only dispersants:

In case of degradation of the dispersant as the only organic material we'd like to suggest the following "in-and-output balance" concerning oxygen and its relation to time:

$$(O_2)_t = (O_2)_{t_0} + (O_{2e}) - (O_{2c}) - (O_2)_{atm}$$

(O_{2e}) = Concentration of oxygen coming in dissolution = (bubble speed/Volum).t
 $= (r(O_2)/V).t$

(O_{2c}) = Concentration of oxygen spent in dissolution = $(r_c(O_2)/V).t$

$(O_2)_{atm}$ = Concentration of oxygen that will be lost to the atmosphere.
 Following the evolution of the data of the concentration of oxygen we assume that the emerging air will contain no oxygen at all.

The oxygen is consumed by respiration of the microorganisms during the process of degradation of the organic material (dispersant). We assume that this will go proportionally to the concentration of the microorganisms and organic material respectively.

$$(O_2)_{consumed} = (O_2)_{resp.} + (O_2)_{deg.} = K_r.C_b + K_d.C_s \quad (1)$$

were:

C_b and C_s are the concentration of the microorganisms and dispersant respectively.

K_r and K_d are the coefficients of proportionality for respiration and degradation of the dispersant, in relation to the necessary oxygen.

The velocity in consumption of oxygen is:

$$(r_c) = d(O_{2c})/dt = K_r.dC_b/dt + K_d(-dC_s/dt)$$

The negative symbol is the result of the fact that (dC_s) is getting negative through time while (O_{2c}) is becoming positive.

Due to the fact that sea water is lacking in microorganisms the result obtained by the Thomas method is negative and the quantity of nutrients is rather small in sea water, we assume together with Larson (21), as we have got a similar case, that: $dC_b/dt = K_c$, where K_c is its growth.

Parallel to this we have measured the concentration of the dispersant during its degradation in sea water and this could be now expressed by the equation: $C = a.exp(-b.t^2)$ (2)

whereby a and b are constants or coefficients of integration of each of the dispersants Renex-706 or Renex-714. Accordingly, the consumption of oxygen is expressed by:

$$r_c = K_r.K_c - K_d.a.(-2bt.exp(-bt^2)) \quad (3)$$

the equation (1) therefore becomes:

$$(O_2)_t = (O_2)_0 + ((r_c(O_2)/V) - K_r.K_c).t - 2abK_d.exp(-bt^2)$$

the results obtained have been adjusted by the method simplex using equations of the type: $(O_2)_t = (O_2)_0 + P.t - Q.t^2.exp(-bt^2)$

whereby P and Q are used as parameters. The coefficients "a" y "b" are determined by measuring the concentration of the dispersant (CTAS method (5)) and its results are found by equation of type (2).

The volume of the dissolution is 4.75 l., and $r_{eO_2} = 0.5$ l/min = 276019.2 mgO₂/day.

The value of K_d is obtained from the DTO of each dispersant, and therefore values are derived for the parameter "b" which are compared with the results obtained by other methods. Table (II) shows this.

	$P(\text{mgO}_2/\text{day}.1)$	$Q(\text{mgO}_2/\text{day}^2.1)$	$a(\text{ppm})^*$	$b(\text{day}^2)^*$	$(\text{O}_2)\text{ppm}$
Renex-714	$3.5648.10^{-4}$	$1.1554.10^{-3}$	5.01	$7.406.10^{-5}$	8.8
Renex-706	$8.1499.10^{-4}$	$1.0812.10^{-3}$	4.65	$6.050.10^{-5}$	8.9

Table II: Results of the fitting of the results of table I (columns 2 and 3) for equation (4).

(*) Values obtained by CTAS method.

Studying these results, we conclude that: $K_d.K_c = 5.81094.10^4 \text{ mgO}_2/\text{l.day}$ for Renex-714 and $5.81083.10^4 \text{ mgO}_2/\text{l.day}$ for the Renex-706.

These results show a difference of 20.7% for the Renex-706 and 27.9% for the Renex-714 in comparison with the results obtained by the method CTAS. However used in equation (2) it will lead to a degradation of 92% for the Renex-714 after 221 days. Comparing with the methods CTAS (98.1%) and IR spectroscopy (97.1%) or the CO_2 analysis (84.5%) the results take up an intermediate position. For the Renex-706 a value of 90.7% has been obtained (95.7% for CTAS, 95% for IR spectr. and 80.24% for CO_2 analysis). These differences are explained by the fact that the CTAS and IR spectr. methods determine the so-called "first biodegradation" while the CO_2 method concentrates on the "last biodegradation". Moreover, parts of the dispersant are consumed in the transformation stage into organic material during microorganic growth. Also, sea water retains CO_2 after destroying the marine buffer dissolution.

The maximums and minimums respectively have been calculated as equation 3 and 4 are functions of each. Table III shows the results with the different values of the coefficient "b".

	RENEX-714		RENEX-706	
	CTAS	O_2 Conc.	CTAS	O_2 Conc.
$t(\text{maximum consum}) = \sqrt{1/2b}$	82.2days	96.8days	90,9d.	101.8 d.
$t(\text{conc. minimum}) = \sqrt{1/b}$	116.2 "	136.9 "	128.5d.	143.9 d.

Table III: Values of coefficient "b" obtained for different methods.

Our conclusion is that in the beginning there is a growing consumption of oxygen with at the same time a maximum growth of microorganisms. Then, its growth is slowed down and stops because the amount of organic material decreases and the population of microorganisms stabilizes. Finally the population of microorganisms diminishes due to complete lack of organic material (progressive process) and consumption of oxygen is reduced.

3.2.- Dissolutions of the dispersant and crude-oil:

The results corresponding to the variation in concentration of oxygen in the dissolution are shown in table I (columns 4 and 5) and could be compared with the results of the same dispersants without the crude. It can be observed that the concentration of oxygen develops in a similar way, although with inferior concentration of oxygen (see item 3.1). These results could be correlated to the phenomena mentioned before studied in sea water which are the already suggested and the degradation of the crude. Through measuring the amount of released CO_2 we have found out that the extent of transformation of crude is rather limited.

The dispersant, in absence of crude, degrades alike and into a similar extent. This is analysed by IR spectroscopy (22 to 25). The degradation of the crude can be formulated now using an equation of the first degree, with method of measurement the CO_2 released.

Consequently:

$$(\text{crude})_t = (\text{crude})_0 - b' \cdot t$$

therefore, the velocity in consumption of oxygen will be:

$$r_{\text{CO}_2} = (d(\text{O}_2)_{\text{cons}}/dt) = K_r \cdot dC_b/dt + K_d \cdot (-dC_s/dt)$$

Whereby: C = Concentration of dispersant

C^s = Concentration of the crude-oil

K_d^c and K_d' are the coefficients of proportionality for degradation of the dispersant and crude-oil respectively.

(O_2) = Concentration of oxygen

$(-dC_c/dt) = b'$

The equation (3) can be reduced to: $r_c = K_r \cdot K_c - 2abK_d t^2 \cdot \exp(-bt^2) - K_d' b'$ (5)

and the equation (4) in:

$$(\text{O}_2)_t = (\text{O}_2)_0 + ((r_{\text{eO}_2}/V) - K_r \cdot K_c - K_d' \cdot b') \cdot t - 2abK_d t^2 \cdot \exp(-bt^2) \quad (6)$$

By using equations of this type for adjusting the experimental datas (symplex method), the following values for the constants are obtained. Table IV shows the results:

	$P(\text{mgO}_2/\text{l.day})$	$Q(\text{mgO}_2/\text{l.d}^2)$	$a(\text{ppm})^*$	$b(\text{d}^{-2})^*$	$b'(\text{mgCr/l.d.})^{**}$
Renex-714	$-5.8089 \cdot 10^{-3}$	$-1.0582 \cdot 10^{-3}$	4.96	$8.133 \cdot 10^{-5}$	$1.17 \cdot 10^{-3}$
Renex-706	$2.4128 \cdot 10^{-3}$	$-1.0656 \cdot 10^{-3}$	4.63	$6.220 \cdot 10^{-5}$	$1.40 \cdot 10^{-3}$

Table IV : Results of the fitting of the results of table (column 4 and 5) for equation (6)

(*) Values obtained by IR spectroscopy method

(**) Value obtained by CO_2 released analysis

The coefficients "a" and "b" are obtained from a direct measurement of the dispersant concentration using the IR spectroscopy; the coefficient b' through analysis of the amount of released CO_2 . The coefficient P is broken down into the following addends P' and R , whereby $P' = ((r_e/V) - K_r \cdot K_c)$ and $R = K_d' \cdot b'$. We assume that there is a minimum of crude degradation with regard to the dispersant (other phenomena such as evaporation and sedimentation eliminate most of its dissolution). Crude on the contrary of the dispersant (90% of degradation) shows hardly a 30% in case of the Renex-714 and less than a 20% for the Renex 706. The value of $K_d' \cdot b'$ can be estimated (supposing that P' represents the coefficient P in absence of crude. K_d' is equal to DTO of the crude ($K_d' = 3.645 \text{ mgO/mg Cr-oil}$, assuming that the crude which is being degraded is represented by a C_{18} hydrocarbure). Table V shows the results.

TABLE V

	P	P'	$-K_d' \cdot b'$	b'
Renex-714	$-5.8089 \cdot 10^{-3}$	$3.5648 \cdot 10^{-4}$	$-6.1654 \cdot 10^{-3}$	$1.6915 \cdot 10^{-3}$
Renex-706	$2.4128 \cdot 10^{-3}$	$8.1499 \cdot 10^{-4}$	$-1.5948 \cdot 10^{-3}$	$4.3836 \cdot 10^{-4}$

As you can read from table V there exist a high degree of similarity between the values obtained for the coefficient kinetic b' using the two different methods of analysis (released CO_2 (table IV) and the concentration of oxygen (table V)). In case of the Renex 714 as an agent of emulsion but not the Renex 706. No valid conclusions can be drawn, since our assumption was that microorganism systems behave exactly in the same way. It is based on the fact that the dispersant has been completely degrade; almost in the same way as it will have happen in absence of the crude. Nevertheless it will exert its influence; this is because degradation has taken place and there are also possible signs of toxicity of hydrocarbon in the microorganisms. It has more influence or the emulsion value is of 2.5 to 1.

Equally, taking as a parameter Q, the value of the coefficient " b " for the one and the other dispersant can be calculated and can be compared with the obtained results studying other properties too (IR spectroscopy).

$$b_{(R-714)} = Q/2abK_d = 4.9387 \cdot 10^{-5} \text{ days}^{-2}$$

$$b_{(R-706)} = A/2abK_d = 4.7748 \cdot 10^{-5} \text{ days}^{-2}$$

The differences in the value of " b " in table IV are significant. Consequently, we can conclude by saying that our model hasn't shown an acceptable level of adjustment taking into consideration that the dispersant is the only source of organic material and that better purification and a further elaboration is needed

3.3.- Degradation of the crude emulsified in absence of the dispersant:

In this case it was found that when there was a release of dissolution of more than a 95% of degradation only reached a 9% level (applied method of the amount of released CO_2). Phenomena such as sedimentation and evaporation are considered as being important.

From table I (column 6) we can draw another conclusion: we can say that the air flow of oxygen is superior to consumption and therefore the dissolution is saturated with oxygen giving out the remaining to the surrounding environment. Emulsions of crude in organic material is inferior to 1/3 of the quantity obtained with the dispersants Renex 714 in equal conditions (1/10 with Renex-706).

3.4.- Degradation of dispersants and crude excluding airing:

The results obtained from measuring the concentration of oxygen in winkler bottles (the dissolutions were kept in there) are found in table VI. Given that a concentration of oxygen has become almost zero, the degradation of organic material with regard to each dissolution (as done by other methods for its growth) no kinetic death of microorganisms. This is because of the fact when oxygen has been given out, there is no further basis for microorganisms subsistence.

The phenomena respiration and death will be assumed now:



Studing the results in table VI it seems to be that it must be a kinetic exponential process. However, due to insufficient data no reliable adjustment can be couldn't support it with any further reliable adjustment.

Time (days)	CONCENTRATION OF OXYGEN (ppm)				
	Renex-714	Renex-706	Renex-714 + crude-oil	Renex-706 + crude	Crude oil
0	8.8	8.8	8.8	8.8	8.8
6	6.7	7.4	7.9	8.1	8.4
8	5.2	5.4	6.3	6.5	7.7
14	2.25	3.9	6.6	1.05	6.6
19	1.8	3.3	3.2	0.45	6.1
22	1.5	2.45	2.05	0.4	5.7
26	0.9	1.7	1.67	0.27	5.0
33	0.7	1.25	0.35	0.3	4.6
40	0.4	0.4	0.25	0.3	3.2
47	0.3	0.32	0.25	0.3	2.7
54	0.3	0.3	0.2	0.2	1.5
61	0.3	0.25	0.1	0.2	0.6
68	0.25	0.25	0.1	0.1	0.2

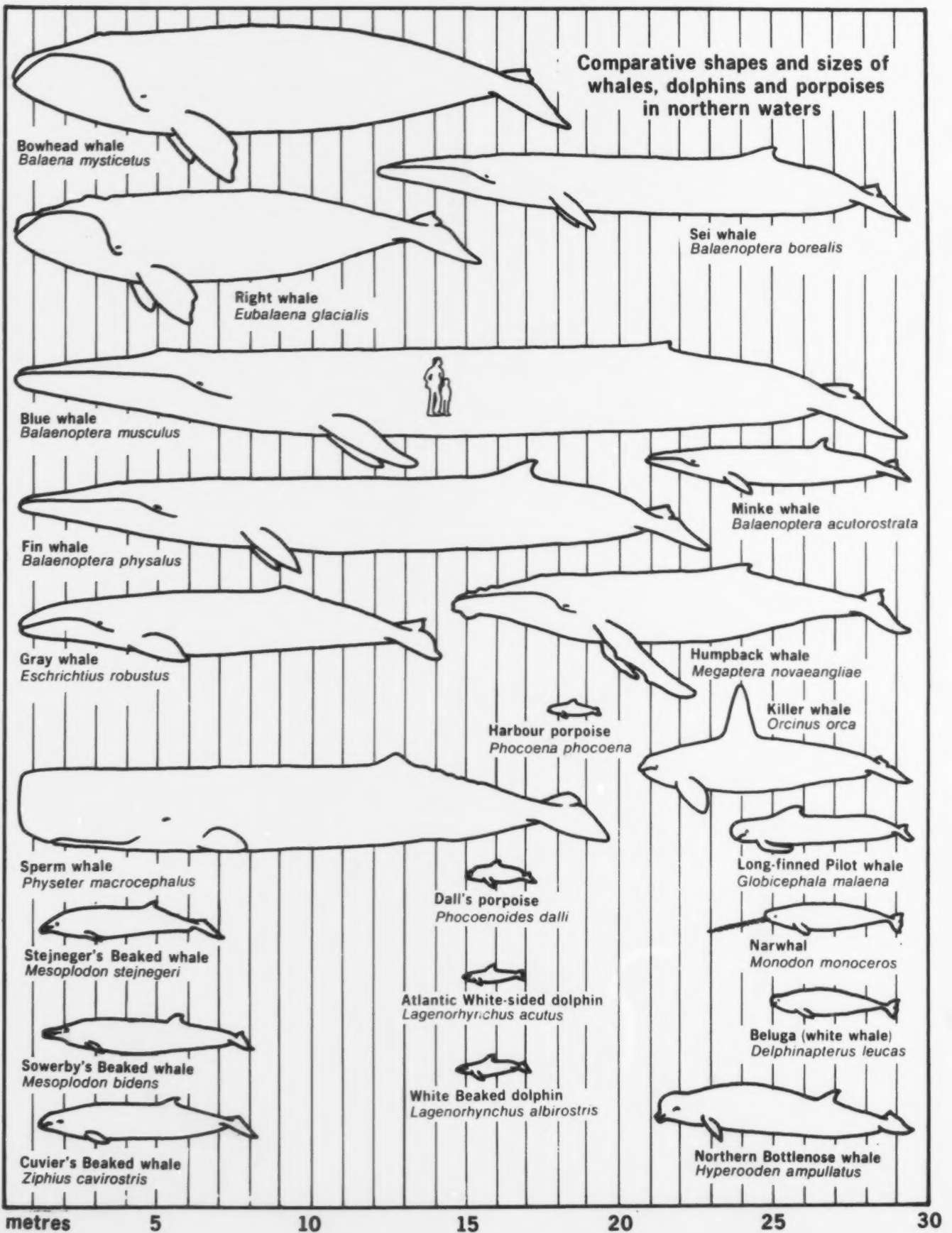
Table VI: Results experimentals of the concentration of oxygen in winklers bottle

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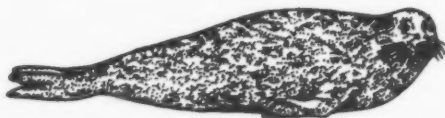
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Comparative shapes and sizes of
whales, dolphins and porpoises
in northern waters



SEALS OF THE ARCTIC AND EASTERN CANADA



HARBOUR SEAL

Phoca Vitulina



GREY SEAL

Halichoerus Grypus



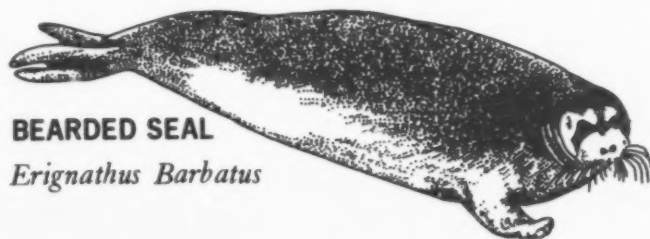
HARP SEAL

Pagophilus Groenlandicus



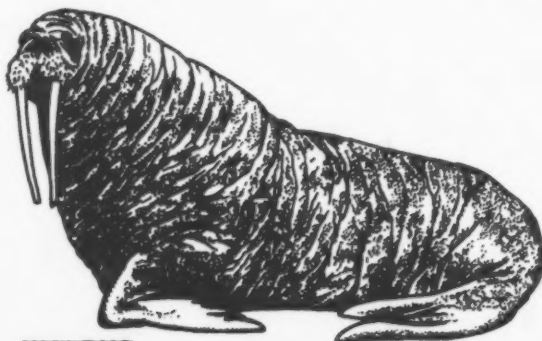
♂ HOODED SEAL

Cystophora Cristata



BEARDED SEAL

Erignathus Barbatus



WALRUS

Odobenus Rosmarus



RINGED SEAL

Pusa Hispada

